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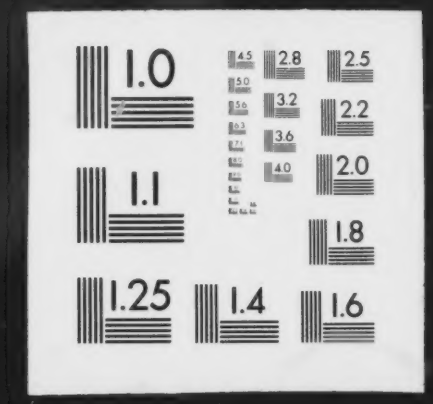

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Battelle Columbus Labs, OH

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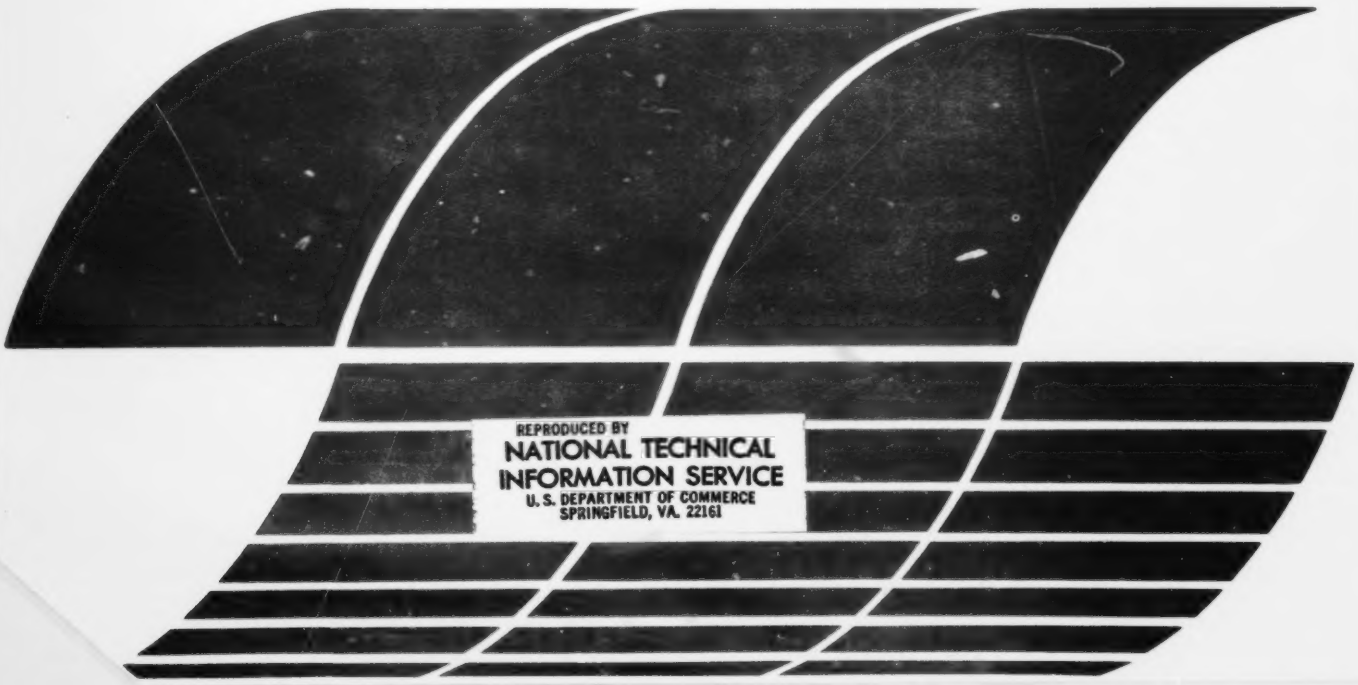
Interim Report

Interagency Energy/Environment R&D Program Report



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16. ABSTRACT

This research program was initiated with the objective of developing methods to identify and measure inorganic compounds in particulate emissions which emanate from sources using or processing fossil fuels.

An extensive literature review was carried out to ascertain prior knowledge on the possible compound forms present in these emissions and to review analytical methodologies. Based on the findings of the literature review, appropriate methodologies were selected for laboratory trial. Concurrent with the method trial work, large masses, 20 to 100 grams, of field samples were collected representative of a range of both coal and oil-fired fly ashes, and the selected methodology development efforts were evaluated on these field samples as well as on synthesized samples.

Fourier transform infrared spectroscopy, x-ray diffraction, and chemical phase separations and analyses are the methods which have provided the most definitive identification of inorganic compounds. The structural findings by these methods are complemented by complete cation-anion chemical determinations. Extensive data on the composition of crude oils, coal and ashes are also presented.

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METHODS FOR ANALYZING INORGANIC COMPOUNDS IN PARTICLES EMITTED FROM STATIONARY SOURCES

Interim Report

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ABSTRACT

This research program was initiated with the objective of developing methods to identify and measure inorganic compounds in particulate matter which emanate from sources using or processing fossil fuels.

An extensive literature review was carried out to ascertain prior knowledge on the possible compound forms and chemical species present in these fly ash emissions and to review and evaluate analytical methodologies applicable for use in the research program. Based on the findings of the literature review, appropriate methodologies were selected for laboratory trial. Concurrent with the method trial work, large masses, 20 to 100 grams, of field samples were collected representative of a range of both coal and oil-fired fly ashes and the selected methodology development efforts were tested on these field samples as well as on synthesized samples.

FT-IR, XRD, and chemical phase separations and analyses are the methodologies which have provided the most definitive identification of inorganic compounds. The structural findings by these methods are complemented by complete cation-anion chemical determinations.

Notable in the methodology development work has been the novel application of infrared spectrometry to inorganic compound identification and, in the analytical data, the findings of relatively high water solubilities of fly ashes, the presence of vanadium oxysulfate as a principal emission form of vanadium from fuel oil combustion and the presence of high sulfates in the fly ashes especially those emitted from fuel oil combustion processes. These are described and documented in detail in the Experimental section of this report.

This report is submitted as an interim report in fulfillment of Contract No. 68-02-2296 under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period January 1, 1977, to July 31, 1978.

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INTRODUCTION

Sources using or processing fossil fuels are among the major contributors to atmospheric particulate pollution. Comparatively little is known about the nature of these particulate emissions other than their mass emission rate, some particle size information and elemental compositions. Even elemental composition data are sparse and incomplete in respect to emissions from sources using or processing fuel oils. Based on the known elemental data, potentially hazardous substances are contained in fossil fuel derived particulate emissions which are released in large tonnages into the atmosphere. However, a full assessment of their health hazards requires knowledge of their chemical form--i.e., how the chemical contents are tied together. Since the major emission sources of fossil fuel derived particulate matter are from combustion processes, it can be assumed that the particulate matter are principally of an inorganic nature. Very little prior analytical effort has been applied to inorganic identification of fossil fuel derived particulate emissions. Identification of inorganic forms of particulates is in certain ways more difficult than identification of organic forms since, although the number of inorganic species may be less, the more commonly used inorganic analytical methods are based on the breaking down of chemical bonds and compounds to ionic forms prior to completing the analyses.

The candidate structural or chemical form determination methods anticipated of being of most value in the identification and measurement of particulate emissions from fossil fuel operations--coal and oil-fired power plants and petroleum refineries--were X-ray and electron diffraction (XRD and ED) and Fourier transform infrared (FT-IR) with supplemental information by electron microprobe (EMP), scanning electron microscopy (SEM), thermodynamic predictions, photoelectron spectroscopy (ESCA or XPS), and Knudsen cell mass spectrometry. These latter two techniques were not investigated in any detail. Obviously, chemical analyses--cation and anion determinations--would be necessary to elucidate and aid in the quantifications of the structural method efforts. Separation techniques--solvent, specific gravity, magnetic, etc.--would be useful to reduce complexity of the diffraction patterns and IR spectra. Also valence state determinations, viz., V^{III}, V^{IV}, V^{V}, ratios in oil fly ash, were anticipated to be needed and utilized to corroborate structural findings. Thermal analyses would be useful in noting species changes during and after sample preparation treatments.

A literature search was carried out to ascertain what methodologies had been developed for fossil fuel emission inorganic particulate compound identification and/or could be modified for such identification. Simultaneously with the literature examination, relatively large masses (20 to 100 grams) of typical samples were obtained for realistic trials of the candidate methods. These efforts, (1) review of methods, (2) obtaining reference samples, and (3) trials of methodologies, have constituted the principal program activities and are described in detail in the Experimental section.

CONCLUSIONS

The extensive literature revealed that very little data are available concerning the compositions of oil-fired fly ash petroleum refinery particulate emissions and, accordingly, less concerning the inorganic forms of these. Considerably more information is known about coal-fired fly ash compositions, derived secondarily from studies directed toward utilization and waste disposal studies of the huge coal fly ash tonnages produced annually. The analytical results given in this interim report and those planned to be obtained during the remaining contract period, in part, fill this information gap on the chemical nature of fossil fuel derived particulates.

Oil-fired fly ashes are to a high degree water soluble, excepting their inert soot-like carbon contents. This water-soluble fraction is composed primarily of sulfates. For example, fly ash from fuel oil derived from Venezuelan crude can contain up to 40 percent vanadium oxysulfate. Much lesser but still significant water solubilities of coal-fired fly ashes have been found with, again, sulfates being the principal anion present in the water soluble fraction.

Health effects studies on potential hazards of fossil fuel fly ash emissions should consider the considerable water solubilities of such emissions and their high concentrations of sulfates. Attention should be focused especially on power plants utilizing fuel oils with high sulfur and vanadium contents. Ambient air measurement studies have shown strong linkage between high vanadium concentrations and fuel oil combustion, with the highest levels of vanadium occurring along the East Coast where fuel oil usage is predominant. The much lower ambient levels of vanadium occurring in the Midwest urban areas, where coal is the major fuel source, indicate that coal usage is not a large factor affecting ambient air vanadium concentrations. This is understandable in the light that, while coals contain 10 to 150 ppm vanadium, an average ash content of 10 percent gives a concentrational factor of ash of only about 10X with much of the ash residing in bottoms or collected by precipitators. Thus coal fly ash, which is emitted as particulates, generally contains 100 to 1500 ppm vanadium. Fuel oils can contain from 50 to 400 ppm vanadium, but with an ash of 0.05 to 0.1 percent, a concentrational factor of 1000X is attained giving oil fly ash values of up to 100,000 ppm. Since most fuel oil combustion units do not utilize control systems, much of this higher concentrational level vanadium is emitted to the atmosphere.

X-ray diffraction, infrared spectrometry, and chemical phase work have proven to be the most useful structural identification mehtods for the fossil fuel derived particulates especially when coupled with complete elemental analyses to provide better quantifications of identified species.

The use of the subtractive capability of Fourier Transform with infrared to identify inorganic sulfate forms is believed to be novel and has proved to be very useful in this methodology development program.

RECOMMENDATIONS

Fly ash samples from petroleum refinery operations should be obtained and analyzed in order to provide a greater representation on which to apply and test the developed methodologies and so as to increase the limited analytical data bank on fossil fuel derived particulate emissions.

Consideration should be given to expanding the program scope to examining particulate matter emitted from nonconventional fossil fuel combustion sources.

A more complete library of reference spectra should be prepared for the Fourier Transform infrared spectrometry work. A replacement of the presently used FTS-14, which has limited storage (~20 low resolution files), by an FTS-10 of increased storage capacity will permit permanent cataloging for storage and retrieval of the needed metal sulfate and oxide reference spectra to facilitate identifications in the samples.

Additional studies should be carried out at a microscopic level to examine single particles for compositions in order to ascertain the chemical forms of trace constituents in the particulate emissions.

More emphasis should be placed on the development of methodologies to obtain more quantitative XRD and FT-IR data.

Finally, particles should be examined for compositions as functions of their surfaces versus depths.

LITERATURE REVIEW

A comprehensive literature review was carried out of prior and ongoing identification studies utilizing computer search of the Chemical Abstracts, APTIC, and Smithsonian Science Information Exchange. Off-the-shelf personal Battelle literature holdings and those contained in specific journals, notably Analytical Chemistry, Analyst, Talanta, Atmospheric Environment, Staub, Fuel, Science, Environmental Science & Technology, JAPCA, and the Industrial Hygiene Association Journal, were searched specifically. Findings have been grouped under the general classifications of coal-fired fly ash constituents, oil-fired fly ash constituents, petroleum refinery emissions, and analytical identification methodologies. The latter includes methods which have not been used for fossil fuel particulate emission analyses but are deemed applicable.

Overall, the literature review revealed that little prior work has been done on the development and application of methods for the determination of the coal ash chemical forms of inorganic particulate emissions from fossil fuel sources as compared to the extensive work done on compositional analyses and organic compound analyses methodology. The paucity of the information on the compositions of oil fly ash emissions and trace elements in fuel oils as contrasted to comparable data on coal fly ash and coals is surprising. However, when the relative ash contents of fuel oils and coals (0.05 and 10 percent, respectively) are considered, this is understandable. Approximately 40 million tons of coal fly ash are produced annually in the United States alone by the burning of some 400 million tons of coal by the utilities. This high ash mass has given rise to usage, control measures, and disposal studies which in turn have required study both of the compositional and the chemical and structural form of the ash. On the other hand, particulate emissions to the atmosphere from oil-fired sources, up to recently at least, have largely not been controlled and the oil-fired fly ash does not pose a solids waste disposal problem.

CHEMICAL AND PHYSICAL CHARACTERISTICS OF FLY ASH FROM COAL-FIRED POWER PLANTS

Coals

The nature and identity of inorganic compounds (mineral species) occurring in coals have been studied extensively over the past 30 years and, although chemical reactions and changes which occur during coal combustion are complex and vary with the fuel and combustion conditions, an examination of the various minerals and chemical combinations of elements found in coals

can give useful insight into the inorganic compounds and chemical phases found in coal-fired power plant fly ash emissions. Coals contain elements, other than carbon, hydrogen, and oxygen, which may be present both as part of the organic structure and as inorganic material from plants or minerals. The principal mineral phases present in coals have been summarized by O'Gorman and Walker[1], Nelson[2], Pringle[3], and many others. The principal forms are listed in Table 1. The banded components of coal--vitrain, clarain, durain, and fusain--which are the end-products of different coalification routes, differ also in the manner in which they reacted to the infiltration of contaminants during the formative period. Vitrain generally is low in impurities, while durain often contains finely disseminated clay minerals, and fusain with its open fibrous structure frequently is rich in many minerals.

The modes of occurrence of minor and trace elements and sulfur and their associations have been discussed by Bethel[4], O'Gorman[1], Zubovic, et al.[5,6] A compilation of these is given for many elements in Table 2. Many minor and trace elements are closely associated with and/or organically bound with the coal substrates, especially the vitrain rather than with minerals or other inorganic constituents. Zubovic, et al.,[7] showed certain elements to have organic affinity of the following order:

$$Ge>Be>(Ba\ Ti\ B\ V)>Ni>(Co\ Y)>Mo>Cu>Sn>Lu>Zn \quad .$$

Compositions of coals have been listed by many.[8,9,10] These vary widely with geographic locality and rank. Typical limits of the major inorganic metals and sulfur present in various coal ranks are given in Table 3. These are arbitrarily given as oxides, but are of the chemical forms given in Table 1.

As can be seen, the variations even within rank are large. Trace metals, as expected, also vary widely in coals. Typical contents for U.S. eastern and western coals have been given in the literature[8,11] and the data in Table 4 are representative of these. More complete data for many trace elements in various coals are given in the Appendix, Tables A-1 to A-3.

Coal Fly Ash

Ash resulting from coal combustion reflects both the mineral content of the coal particles and the combustion conditions. Fuel particles pass through the combustion system with the air stream, burning as they go, frequently with little intercontact, so do not attain equilibrium compositions. As a result, fly ashes are highly heterogeneous materials. The composition and compound nature of coal fly ash have been studied extensively both to find profitable uses and/or suitable waste disposal means for the tremendous tonnages of ash (40 million tons in the U.S.) generated yearly and, more recently, for emission control and pollutant abatement purposes.[12-25] The methods of study have been principally X-ray diffraction, physical separations (magnetic and specific gravity), microscopy (petrography, optical,

TABLE 1. PRINCIPAL MINERAL FORMS OCCURRING IN COAL SEAMS

Form	Minerals	Formula
Silicates	Montmorillonite	$(Mg\ Ca)O \cdot Al_2O_3 \cdot 5SiO_2XH_2O$
	Feldspar	$(Na \cdot K)AlSi_3O_8$
	Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
	Muscovite	$H_2KAl_3\ (SiO_4)_3$
	Chlorite	$(MgFe)_5(Al\ Fe)_2Si_3O_{10}(OH)_8$
Sulfides	Pyrite	FeS_2
	Marcasite	FeS_2
Oxides	Quartz	SiO_2
	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
Sulfates	Gypsum	$CaSO_4 \cdot 2H_2O$
	Jarosite	$KFe_3(OH)_6(SO_4)_2$
Carbonates	Calcite	$CaCO_3$
	Siderite	$FeCO_3$
	Ankerite	$(Ca\ Mg\ Fe\ Mn)\ CO_3$
Chlorides	Halite	NaCl
	Silvine	KCl

TABLE 2. PROBABLE DISTRIBUTION OF MINOR AND TRACE ELEMENTS IN COALS

Periodic Table Grouping	Mineral Association	Coal Association
Li, Rb, Cs		
Li	Most likely with mica	--
Cu, Ag, Au		
Cu	Chalcopyrite Cu-Fe-S	Intrinsic with vitrain, durain
Ag, Au	Argentiferous and auriferous pyrites	Intrinsic - vitrain, durain
Be	Little	Intrinsic - vitrain
Sr, Ba, Ra		
Sr	--	--
Be	Barite - $BaSO_4$, withirate - $BaCO_3$	--
Ra	--	Possibly because well distributed
Zn, Cd, Hg		
Zn	Sphalerite - ZnS	In low concentrations
Cd	Probably with minerals of sulfide type	--
Hg	Probably with minerals since poorly d stributed	--
B	Possibly tourmaline (a borosilicate) and/or in illite	Probably intrinsic - mostly from plant life
Sc, V, Rare Earths	Probably extrinsic with clays or shales	--
Ga, In. Tl	--	Probably intrinsic with coal substance
Cr	--	With coal substance
Ge, Sn, Pb		
Ge	--	Intrinsic - vitrain
Sn	Galena - PbS also PbO	Also with coal substance
Ti, Zr, Th		
Ti	--	--
Zr	$ZrSiO_4$ - zircon	Intrinsic - vitrain
Th	--	--
P, As, Sb, Bi		
P	Fluorapatite	--
As	With mispickels ($FeS_2 \cdot FeAs_2$)	--
Sb	--	--
Bi	--	--
V	Carnotite ($K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$)	Also in the vitrain
Nb, Ta	--	--
Se, Te	Pyrite/marcasite	--
Cr, Mo, W, U		
Cr	--	Primarily with coal substance
Mo	MoS_3 presence correlates with S	--
W	Like Mo	--
U	Like V in carnotite, also uraninite, coffinite	--
F	CaF_2 fluorite also with phosphorus fluorapatite $CaF_2 \cdot 3Ca_3(PO_4)_2$	--
Cl	NaCl partly	Bonded to N_2 atoms in coal substance
Re	--	Intrinsic with coal substance
Co, Ni		
Co	Linnaeite $(Co,Ni)_3S_4$	--
Ni	Pyrite/mariosite, Ni with millerite NiS	--

TABLE 3. MAJOR CONSTITUENTS OF U.S. COALS BY RANK (IN PERCENT)

Constituent	Anthracite	Bituminous	Subbituminous	Lignite
Fixed Carbon	75-90	40-70	30-60	20-50
Volatile Matter	1-10	20-45	15-40	20-50
Ash	5-20	5-25	3-15	5-20
SO_3	1-5	2-12	5-15	4-16
SiO_2	1-10	2-12	3-15	3-15
Al_2O_3	3-15	1-10	1-10	3-15
Fe_2O_3	2-10	0.5-0.5	2-10	1-5
TiO_2	0.1-1.0	0.1-1.0	0.2-2.0	0.2-2.0
CaO	1-5	0.3-3.0	1-5	1-5
MgO	0.2-2.0	0.1-1.0	0.2-2.0	0.2-2.0
Na_2O	0.1-1.0	0.05-0.5	0.05-0.5	0.1-1.0
K_2O	0.2-2.0	0.1-1.0	0.2-2.0	0.2-2.0

TABLE 4. APPROXIMATE CONTENTS OF TRACE ELEMENTS IN U.S. COALS (RESULTS IN PPM)

Element	Eastern	Western	Element	Eastern	Western
As	15	2	Mo	8	5
Be	2	1	Ni	22	5
Cd	3	0.1	Pb	40	17
Co	10	7	Sb	1.5	0.6
Cr	14	8	Se	2	1.5
Cu	14	20	Sn	5	5
F	60	60	V	33	20
Ge	10	3	Zn	315	11
Hg	0.2	0.06			
Mn	53	45			

scanning, electron), thermal, and to a lesser extent infrared. Extensive data are available on the compositions of coal ashes, variations in compositions as a function of particle sizes and on pathways of selected elements from the fuel to residences in various ash beds to escape to the atmosphere. Changes in phase of minerals in coal have been followed via low temperature electronic (plasma) and higher temperature ashing techniques.[26-29] The electronic ashing process is lengthy, taking up to 200 hours to come to a relatively steady state weight change, but does provide a useful means of predicting phase changes during coal combustion processes.

Although wide variations exist in fly ashes derived from conventional coal-fired power processes, they have been characterized generally as consisting of heterogeneous finely divided, highly siliceous, spherical-shaped particles containing residual unburned carbon, magnetic and nonmagnetic iron compounds, some alkali and water-soluble components. Most coal fly ashes are described as 5 to 15 percent of crystalline material and 70 to 90 percent glass, plus unburned carbon. The crystalline components principally have been identified as quartz, 1 to 5 percent; mullite, 5 to 15 percent; hematite, 1 to 3 percent; and magnetite, 1 to 10 percent. The remaining glass has a composition range generally given as: SiO_2, 50 to 60 percent; Al_2O_3, 20 to 35 percent; Fe_2O_3, 5 to 12 percent; CaO, 1 to 10 percent; MgO, 2 to 5 percent; Na_2O, 0.5 to 1 percent; K_2O, 2 to 5 percent; and TiO_2, 1 to 2 percent. (In the work described later in this report, it is shown that certain coal fly ashes contain high concentrations of metal sulfates and substantial water-soluble components.)

Studies of mineral phases or inorganic compounds largely have been confined to the higher metal concentrational contents of fly ashes with only very limited examinations of the possible states or chemical combinations of the lower concentrations Ni, Co, V, Cr species, etc. Some work has been done on these lower concentrational metals using techniques such as electron microprobe and scanning electron microscopy equipped with X-ray readout to ascertain elemental interrelations or empirical formulas. Additionally, studies of fly ash particle surfaces have been carried out by surface techniques including ESCA, Auger, and EMMA. However, these latter techniques are relatively insensitive for metallic components due in part to their presence in the bulk rather than the surface of particles. These techniques are well summarized by Keyser, Natusch, Evans, and Linton.[30]

CHEMICAL AND PHYSICAL CHARACTERISTICS OF OIL-FIRED POWER PLANT FLY ASH

Fuel Oil

Fuel compositions used in power production vary depending on the origins of the crude (see Appendix Tables A-10 to A-15), the minerals and metals picked up as the crudes are transported to the refineries, the contamination (or loss--desulfurization, etc.) occurring in the refining process, and on the compositions of fuel additives, if used. Several metal contaminants such as iron, nickel, and vanadium occur in crude oil as organometallic compounds generally of the porphyrin type. Sulfur contents of fuel

oils vary depending on the source of the originating crude and the subsequent refining process. While the concentration of sulfur varies widely even in a given geographic area or oil field, most crudes contain from 1.0 to 2.5 percent sulfur present mostly as complex organic sulfides, some elemental sulfur, and possibly as sulfates. Generally residual fuel oils contain about twice the sulfur of the originating crude, but this is dependent on the refining process. Ash-forming constituents in the crudes go through the refining process practically unchanged and are concentrated in the bottom, with residual fuel oil No.6 or Bunker C comprising the residual or bottoms from distillation of crudes. The principal ash-forming elements found in crude oil as given by Bowden, et al.,[31] are listed in Table 5. Vanadium, which occurs mostly in asphaltic-base crudes is present principally as an oil-soluble porphyrin complex. These are very temperature stable and so are retained in the residual during the refining process. Thermal ashing of heavy residual fuels results in an ash percentage varying generally from 0.01 to 0.1 percent. Fuel additives containing inorganic metals such as Mg, Mn, Al, etc., when used, of course increse this thermal ash percentage.

TABLE 5. PRINCIPAL ASH-FORMING ELEMENTS IN CRUDE OIL

Element	Type	Solubility in Oil	Probable Chemical Form
Aluminum	Inorganic	Insoluble	Complex alumino-silicates in suspension
Calcium	Organic	Soluble	Not identified
	Inorganic	Insoluble	Calcium minerals in suspension; calcium salts in suspension or dissolved in emulsified water
Iron	Organic	Soluble	Possible iron porphyrin complexes
	Inorganic	Insoluble	Finely sized iron oxides in suspension
Magnesium	Organic	Soluble	Not identified
	Inorganic	Insoluble	Magnesium salts dissolved in emulsified water or in suspension in microcrystalline state
Nickel	Organic	Soluble	Probable porphyrin complexes
Silicon	Inorganic	Insoluble	Complex silicates and sand in suspension
Sodium	Inorganic	Insoluble	Largely sodium chloride dissolved in emulsified water or in suspension in microcrystalline state
Vanadium	Organic	Soluble	Vanadium porphyrin complexes
Zinc	Organic	Soluble	Not identified

Fuel Oil Fly Ash

The above mineralogical or thermal ash content compositions and percentages of fuel oils do not represent the total particulate contents of oil-fired fly ashes. These include carbonaceous material (partially combusted carbon) and nitrogen and sulfur compounds. The metallic salts, sulfur and nitrogen compounds, which have as their sources the crudes from which the fuel oils were derived plus impurities occurring during the handling, transport, and refining of the crudes, constitute the basis for inorganic compounds found in fly ash. The carbonaceous products are principally of a soot-like substance consisting largely of amorphous or partially graphitic carbon and can constitute up to 70 percent of the mass of the fly ash. Table 6 taken from Miller, et al.,[32] lists many possible metal ash constitutents formed during fuel oil combustion and the melting points of their oxide or sulfate forms.

The ash constituents of course are not simply oxide or sulfate metal salts. For instance, vanadium complexes in the fuel oil droplets decompose during combustion and oxidize in steps, possibly to V_2O_5. However, the vanadium may react with other metal oxides (Ni, Fe, Na, Ca, Mg, and sulfur) present in the oil or oil additive to form a variety of vanadate salts. Vanadium compounds in fly ash from oil-fired units have in several instances been found to be water soluble to a large extent--see Experimental section. Fly ash constituents vary from surface to bulk and surface compositions have been studied by several techniques.[30] This can be important in characterizing the porous, high surface area ashes commonly encountered in oil-fired fly ashes.

Factors other than fuel composition which affect the nature and quantities of fly ash emitted from oil-fired power plant burners include the manner in which the fuel is sprayed and vaporized, the air-to-fuel ratio, the residence time in the combustion zone, fuel additives, and the flame or combustion zone temperature. McGarry and Gregory[33] in a study of particulate emissions from oil fired boilers for power generation found that an important factor governing the size, quantity, and nature of the particles is the degree of atomization. Their study showed that poor atomization results in large fly ash particles and a high particulate loading since the droplets of fuel may be large and difficult to combust completely. Conversely, with small droplets more complete combustion is attained and usually the particle size of the fly ash emissions is small as well. Goldstein and Siegmund[34] in their study of the influence of heavy oil composition and boiler combustion conditions on particulate emissions showed, in their tests using conventional high-sulfur and low (0.3 percent) sulfur oils, that there was an optimum level of excess air which corresponded to minimum particulate emissions. Above and below that level particulate emissions increase. Their study showed that 60 percent excess air was optimum for particulate burnout, but this was not optimum for boiler efficiency. Normal practice is to operate the boiler with the minimum of excess air. Combustion chamber residence time also is an important factor in governing the quantities and characteristics of particulate emissions from boilers--the longer the period in the combustion zone, the less emissions and the smaller the size of the particulate emissions. With longer residence periods the carbonaceous particles

TABLE 6. POSSIBLE VANADATE COMPOSITIONS FORMED DURING COMBUSTION OF RESIDUAL OIL*

Compound	Melting Point, F	Compound	Melting Point, F
V_2O_5	1274	$2NiO \cdot V_2O_5$	>1652
$3Na_2O \cdot V_2O_5$	1562	$3NiO \cdot V_2O_5$	>1652
$2Na_2O \cdot V_2O_5$	1184	$Fe_2O_3 \cdot V_2O_5$	1580
$10Na_2O \cdot 7V_2O_5$	1065	$Fe_2O_3 \cdot 2V_2O_5$	1571
$Na_2O \cdot V_2O_5$	1166	$MgO \cdot V_2O_5$	1240
$2Na_2O \cdot 3V_2O_5$	1049	$2MgO \cdot V_2O_5$	1535
$Na_2O \cdot 2V_2O_5$	1137	$3MgO \cdot V_2O_5$	2175
$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$	995	$CaO \cdot V_2O_5$	1145
$Na_2O \cdot 3V_2O_5$	1150	$2CaO \cdot V_2O_5$	1432
$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	1157	$3CaO \cdot V_2O_5$	1860
$Na_2O \cdot 6V_2O_5$	1215		

*Compiled from a number of sources.

are burned with a greater efficiency resulting in lesser amounts of particulate emissions and in smaller size particles.

All of these factors, fuel composition, air-to-fuel ratio, combustion zone temperature, time of residence in the combustion zone, plus use of additives, affect the nature, quantity, and size distribution of particulate emissions from utility boilers. For these reasons methodologies to determine inorganic compounds in oil-fired power plant emissions should take into account the varying nature of these substances. For example, under a given operating condition and with a certain fuel type, a highly oxidized form of vanadium might be found present in the emissions, while under other operating conditions the vanadium can occur in a more reduced form.

Certain physical differences can be applied to oil-fired power plant ash particulate emissions which distinguish them from coal-fired power plant emissions. Some of these are pointed out by Cheng, et al.,[24] who described oil fly ash particles as black, rough, honeycomb-like structures generally of irregular spherical shape, while coal fly ash particulates are characterized as having smooth ball-like surfaces of a regular spherical shape. Cheng, et al., go into further detail on their descriptions, but it seems apparent that many of the finer details they describe are unique to the sample or sample types being examined. While Cheng, et al., describe the oil-fired fly ashes as rough, porous, opague spheres, Goldstein and Siegmund[34] characterize them as cenospheres. The cenospheres are formed from the residues of spray droplets from which, on passing through the flame,

their volatile compounds vaporize and fragments crack from nonvolatile compounds with both of these burning in the vapor phase around the droplet. The nonvolatile carbonaceous residues, roughly the size of the original droplet, which forms a solid skeletal particle and can be full of void spaces, they call cenospheres.

In contrast to most coal fly ash particles which generally are smooth-surfaced, glassy spheres or cenospheres, oil-fired fly ashes generally are more porous, roughly spherical in shape, and can vary quite widely in overall chemical compositions, but to a large extent the carbon in oil-fired fly ash is of a soot-like form. Due to the high combustion process organic compounds are essentially absent in oil and coal-fired fly ashes.

PETROLEUM REFINERY EMISSIONS

The petroleum refining industry is a major fuel consumer, using about 10 percent of the energy in the crude for the myriad separations, fractionations, and other processes which result in their intended end products. The principal origin of emissions from petroleum refineries is the crude oil which represents over 90 percent of the material input to the operations. The raw crude oil as received by a refinery is a mixture of mostly hydrocarbons of varying molecular structure but also contains water, brine, sludge, sulfur compounds, some metals and nitrogen compounds.

It is difficult to generalize about refinery operations and resultant emissions since no two refineries are alike, with extreme variances in the complexity of the processing utilized and the end-products produced. Further variances are introduced by the crudes--what is done to refine one type crude may not be practical for others. In general the older refineries are less complex and produce the fewest petroleum products. However, many of these refineries are being remodeled and reequipped to produce a larger range of products and devices are being added to control pollutant emissions. The principal products of oil refining are gasoline and fuel oils and, since the needs for these are increasing rapidly, refineries will continue to grow as a major energy consumer and as a potentially even larger source of atmospheric emissions.

The exact nature and quantities of these emissions are difficult to pinpoint because of the aforementioned variances in raw materials compositions (mostly crudes), complexity of operations and refining processes, age, and technological sophistication of the plants and lack of data in the literature on specific emissions measurements.

The compositions of crudes, the principal sources of pollutants, are given in Tables A-1 and A-2. An indication of the quantities of emissions by pollutant is given in Table 7 and by process in Table 8.

Petroleum refinery emissions arise from a diverse number of process operations as well as from a wide array of miscellaneous operations such as storage, handling, spillage, incineration of wastes, leaks, flares, treating

TABLE 7. ESTIMATED EMISSIONS FROM 262 REFINERIES (1969)[35]

Pollutant	Emissions, 1000 tons
Sulfur oxides	2200
Nitrogen oxides	61
Hydrocarbons	2300
Particulates	55
Carbon monoxide	2420

and blending operations. Smoke (unburned HC), particulate matter, hydrocarbons, and other gaseous substances, mostly oxides of sulfar and nitrogen, constitute the major types of emissions released by oil refineries. Although refineries vary greatly in the relative complexities of processes employed, the major operations are: separation, conversion, treating, and blending. The catalytic cracking unit is one of the principal sources of pollutant emissions in refineries with the regenerator being the largest offender. Particulate emissions can be reduced by control measures such as use of electrostatic precipitators or cyclones, but efforts to control particulate emissions generally have not received the emphasis as efforts to reduce sulfur compound and hydrocarbon emissions.

Contrary to finding fairly extensive data on coal-fired fly ash emissions and to a lesser extent on oil-fired fly ash emissions, no data were obtained from the literature on the specific compositions of particulate species emitted from refinery operations. Since the catalytic cracking operation has been cited as being a major source of particulate emissions, initial sampling possibly should be done there to obtain samples for use in developing and establishing inorganic compound methodologies.

ANALYTICAL METHODOLOGIES FOR INORGANIC COMPOUND IDENTIFICATION

The literature abounds with analytical methodology descriptions and applications to inorganic particulate pollutant analyses. The great majority of these publications and references describe and/or are applied to the elemental and anionic contents of pollutant samples. No attempt has been made to list these here since they have been reviewed in detail elsewhere in the literature and in EPA reports[36-48], and since their applications to inorganic particulate compound methodology are mostly of a support role, i.e., to provide data on the overall elemental, cation, and anion groupings present in samples and sample fractions.

Comparatively, methods applicable to inorganic compound or chemical form identification and analysis are few, and descriptions of these applied to pollutant samples are quite limited in the literature and in ongoing research and development activities. This lack of attention given to inorganic compound identification in pollutants is unusual in view of frequently declared

TABLE 8. EMISSION FACTORS FOR PETROLEUM REFINERIES

		Emission Factor
A. Boilers and process heaters	#Hydrocarbon/1000 bbl oil burned	140
	#Hydrocarbon/1000 ft^3 gas burned	0.026
	#Particulate/1000 bbl oil burned	800
	#Particulate/1000 ft^3 gas burned	0.02
	#NO_2/1000 bbl oil burned	2,900
	#NO_2/1000 ft^3 gas burned	0.23
	#CO/1000 bbl oil burned	negligible
	#CO/1000 ft^3 gas burned	negligible
	#HCHO/1000 bbl oil burned	25
	#HCHO/1000 ft^3 gas burned	0.0031
B. Fluid catalytic units	#Hydrocarbon/1000 bbl of fresh feed	220
	#Particulate/ton of catalyst circulation	1.8(a)
	#NO_2/1000 bbl of fresh feed	63
	#CO/1000 bbl of fresh feed	13,700
	#HCHO/1000 bbl of fresh feed	19
	#NH_3/1000 bbl of fresh feed	54
C. Moving bed catalytic cracking	#Hydrocarbons/1000 bbl of fresh feed	87
	#Particulate/ton of catalyst circulation	4(b)
	#NO_2/1000 bbl of fresh feed	5
	#CO/1000 bbl of fresh feed	3,800
	#HCHO/1000 bbl of fresh feed	12
	#NH_3/1000 bbl of fresh feed	5
D. Compressor internal combustion engines	#Hydrocarbons/1000 ft^3 of fuel gas burned	1.2
	#NO_2/1000 ft^3 of fuel gas burned	0.86
	#CO/1000 ft^3 of fuel gas burned	negligible
	#HCHO/1000 ft^3 of fuel gas burned	0.11
	#NH_3/1000 ft^3 of fuel gas burned	0.2
E. Miscellaneous process equipment		
1. Blowdown system		
a. With control	#Hydrocarbon/1000 bbl refinery capacity	5
b. Without control		300
2. Process drains		
a. With control	#Hydrocarbon/1000 bbl wastewater	8
b. Without control		210
3. Vacuum jets		
a. With control	#Hydrocarbon/1000 bbl vacuum distillation capacity	negligible
b. Without control		130
4. Cooling towers	#Hydrocarbon/1,000,000 gal cooling water capacity	6
5. Pipeline valves and flanges	#Hydrocarbon/1000 bbl refinery capacity	28
6. Vessel relief valves	#Hydrocarbon/1000 bbl refinery capacity	11
7. Pump seals	#Hydrocarbon/1000 bbl refinery capacity	17
8. Compressor seals	#Hydrocarbon/1000 bbl refinery capacity	5
9. Others (air blowing, blend changing and sampling)	#Hydrocarbon/1000 bbl refinery capacity	10

(a) With electrostatic precipitator.
(b) With high efficiency centrifugal separator.

needs for such information in health and toxicity assessment studies. Several reasons can be cited for this anomaly, but the principal cause is the relative difficulty of inorganic compound identification of samples as complex and heterogeneous as are pollutant emission particulates. The commonly and readily used techniques for analysis of inorganic constituents consist of initially breaking samples down to their ionic forms and/or utilizing the atomic characteristics of the samples' constituents and then isolating individual elements, cation, or anions, chemically or spectrally, for identification and quantification. This is in contrast with the more commonly used organic species analysis methods which utilize the molecular or molecular-fragment properties of the samples for organic constituent identification. These of course are generalizations; since with selected sample dissolution the valence state of certain elements can be retained and quantified, and many inorganic species have unique molecular spectral characteristics and specific crystalline forms. However, the use of these elemental and compound specific techniques for inorganic species identification have not been exploited to any great degree on complex pollutant emission samples. Inorganic compound identification and analyses of pollutant emission samples, what little has been done, has relied mostly on XRD techniques plus morphological characterization of sample component recognition, from the microscopy-instrumented tools of SEM, STEM, and EMP wherein microscopic viewing can be aided by elemental analyses of the viewed particle or particle groupings, and recently the surface identification techniques of ESCA, etc.

The review of literature, search of ongoing R&D efforts, and discussions with leaders in the field of pollutant analyses reveal the following list of techniques and methodologies as most useful for identification of inorganic compounds in particulates emitted from fossil fuel sources:

(1) X-ray diffraction

(2) Infrared spectrometry

(3) Microscopy - optical, electron, petrographic, scanning electron, scanning electron transmission, electron microprobe, and chemical

(4) Surface techniques - ESCA, Auger, SIMS, and IMA

(5) Chemical phase - valance state, separations

(6) X-ray fluorescence

These are discussed in some detail below and their applications to coal and oil-fired power plant particulate and refinery emissions are described. However, as stated elsewhere, very little information is available on oil-fired power plant particulate emissions chemical characterizations, even including compositions.

X-Ray Diffraction

X-ray diffraction methodologies have been used extensively to determine the chemical structure of fossil fuel fly ashes with the referenced publications being among the more thorough studies reported.[1,19,23,49] No XRD studies of oil-fired fly ash emissions were found, although selected studies have been made of oil ash boiler corrosion deposits. The coal ash studies, principally of products of pulverized fuel, have shown fly ash to be comprised of from 5 to 25 percent crystalline products and 75 to 95 percent glass. The crystalline components vary depending on the fuel origin--for instance, a range of British and U.S. fly ashes studied by Simons and Jeffrey[49] were found by XRD analysis to have the following principal components:

	British Coal Ashes	U.S. Coal Ashes
Quartz	1-6.5%	0-4%
Mullite	9-35%	0-16%
Magnetite	∿5%	0-30%
Hematite	∿5%	1-8%

Lime (CaO), anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), and dicalcium ferrite ($2CaO \cdot Fe_2O_3$) also were found in lesser amounts. Using magnetic separations and chemical solution techniques to further examine the iron-containing fly ash components the following distributions were found in several coal fly ash samples:

Magnetic iron (mostly magnetite and lower amounts of hematite)	∿20%
Nonmagnetic iron (dicalcium ferrite)	∿5%
Soluble iron ($FeSO_4$)	∿1%
Silicate iron	∿4%

Several investigators used density (float-sink) techniques to examine various fractions of fly ashes. However, as judged by compositional analyses, little enrichment of chemical species were attained, attributable to the very heterogeneous nature of coal fly ash particles and to the presence of cenospheres which contain light and heavy phases. Several investigators used synthetically prepared standards to aid in interpreting the XRD patterns of coal fly ash samples. These were made up of the principal minerals found in coal (see Table 1) and were fired at elevated temperatures or passed through an oxygen-coal gas flame. The standards prepared this way were found to correspond closely in appearance with those found in commercial glasses.

Based on the work reviewed, the principal crystalline phases in coal ash--quartz, mullite, magnetite, and hematite--can be identified by XRD aided by the use of synthetic standards. Most of the iron present in coal ash occurs in separate iron-rich particles and these too can be separated and identified. The glassy particles of coal ash, largely SiO_2, Al_2O_3, and Fe_2O_3, may be chemically extracted, as has been done with ceramic materials, and the composition of the glass phase determined by chemical means. No XRD work has

been reported on fly ash emissions from oil-fired power plants. However, as can be seen later in the Experimental work section of this report, the chemical nature of these are quite different from the coal ashes. XRD studies of the oil-fired fly ashes should be of considerable value in showing the chemical forms of the important vanadium, iron, and nickel species.

Other than as described above and specialized applications such as free-silica analysis and asbestos identification, X-ray diffraction has not been used extensively in particulate analysis. However, with increasing concern regarding the form of toxic compounds, XRD may play an increasingly active role. One limitation to XRD identifications is the lack of a simplified and valid reference library. There are some 30,000 materials cataloged in the JCPDS-International Center for Diffraction Data. This represents a difficult search problem to identify unknown patterns based on d-spacings and line intensities. Further, some of the data given in the reference file was obtained using impure materials and/or materials in a hydration or crystalline state other than listed. This leads to improper identifications.

Despite these problems, X-ray diffraction remains a key technique for the identification of inorganic compounds in particulate pollutant sample catches and development work, as described by later workers[50-54], indicates that XRD analyses can provide good compound identification.

Infrared Spectroscopy

Infrared techniques have been explored to some extent for use in pollutant analyses, but have not been utilized widely for detailed characterization of fly ashes. Blanco[55] examined dust particulates by infrared spectrometry and found them to consist mostly of the mineral species present in soils and outcroppings. O'Gorman[1] used infrared analysis coupled with X-ray diffraction to follow the mineralogy of coals through low temperature ashing processes. Again, the IR identification consisted principally of the minerals and mineral groupings found naturally in coals and higher oxidation products of these. Both Blanco and O'Gorman point out problems of spectral overlap and inadequate sensitivty. These problems are alleviated considerably by the use of a Fourier transform spectrometer. Cunningham, et al.,[56] using a Digilab Model FTS-14 spectrometer over the spectral range of 400 to 3600 cm^{-1} with an 8 cm^{-1} resolution, measured many of the major chemical constituents of ambient samples. From known reference spectra, assignments of 28 species were made. However, in this work no accounting was taken for spectral alterations due to waters of hydration, mixed sulfates, band splittings due to crystal structure and other factors which complex the identifications. The importance of these factors is discussed in more detail later.

Fourier Transform infrared systems differ from conventional dispersive infrared spectrophotometers in that conventional infrared spectroscopy uses a monochromator to generate the spectral information, whereas an interferometer is used for this purpose in Fourier Transform infrared spectroscopy. The use of an interferometer to generate spectral information in the form of an interferogram (light intensity versus time) necessitates a second

difference between the two types of infrared spectroscopy. This difference is that FT-IR systems use a dedicated digital computer to obtain the Fourier Transform of the interferogram, converting it to a conventional infrared spectrum (light intensity versus wavelength or frequency). These two differences lead to the following two major advantages of FT-IR over conventional infrared spectroscopy:

- An interferometer results in a substantial gain in energy or light throughput as compared to a monochromotor. This gain in energy results from the elimination of the dispersive device since all wavelengths of light are examined simultaneously in an interferometer and no energy is lost (as in a dispersive instrument by examining the light one wavelength at a time). This additional energy can be used in one of several ways: (2) for faster scan speeds (as fast as 0.6 sec), (b) for up to a 30-fold increase in signal-to-noise ratio, and (c) for 10^2-10^3 greater sensitivity.

- The availability of a dedicated computer offers several major data-handling advantages. Not only can spectra be ratioed against each other to remove absorption bands due to background materials, but the computer can be used to perform spectral arithmetic. Thus, spectra can be added or subtracted from each other and also multiplied or divided. In this way, the spectra can be adjusted in size, and unwanted components can be removed from the spectra without the necessity of chemical separations. This ability to utilize a computer is not unique to Fourier Transform spectroscopy, i.e., in theory a computer could be attached to a conventional dispersive infrared spectrophotometer. However, in practice, this is rarely done, whereas all Fourier Transform systems use a computer. Thus, from a practical standpoint, the use of a computer is a major advantage in FT-IR systems.

The applications of FT-IR to inorganic compound identifications have been described by Henry, Mitchell and Knapp[57] and Jakobsen, Gendreau, Henry, and Knapp[58] and are detailed later in the Experimental section.

Microscopy Instrumental Methods

The instrumental techniques of microscopy, scanning electro microscopy (SEM), electron microprobe (EMP), scanning transmission electron microscopy (STEM), electron microscopy microanalyzer (EMMA), and IMA (ion microanalyzer) all have in common a capability to focus on or "see" a very small area of a sample and, in addition to giving a morphological view of the area under the beam, provide elemental compositional data usually via an energy dispersive X-ray analyzer (EDXA). (The IMA gives a mass-sorted signal.)

Several investigators have used one or a combination of these instruments to examine various types of particulate pollutants including coal fly ashes.[24,59-67] Since pollutant samples, especially fly ashes, are highly heterogeneous in size and in composition within a given size distribution, the use of the techniques is tedious even with computer controlled readout. The analytical responses obtained are subject to variation due to such factors as interelement, background, matrix, particle mass, and geometry effects and require fairly complex corrections for quantitative analyses.

Despite these problems, since the focusing beam is highly localized a very good detectability can be obtained for many elements. (With EMP for example, if 100 ppm is detected in a 10 μm^3 volume, this equates to a detection of 1×10^{-14} grams in a material of average density.) Of course the analytical data obtained are elemental, not species nor compound in nature. However, when all elements are scanned in a given area, as on a single particle or particle group, a stoichiometric relationship can be derived and related to compound form. This approach may well be the best technique for determining the chemical association of low concentrations of key metal impurities such as Ni in coal ash at 200 ppm, etc.

ESCA

ESCA has been given increasing attention in examining the composition and chemical states of pollutant species, principally in ambient atmospheric particulate samples.[68-78] For the exciting X-ray photon energies in common use, the outer 10 to 20 A of a sample are probed, and this can represent both an advantage and a disadvantage. There are many problems associated with the use of ESCA techniques, but since both the chemical state and chemical composition are determined, it can provide invaluable (although not always easily interpretable) information regarding particulate pollution composition.

Linton, et al.,[68] using ESCA plus other surface analysis techniques including IMA, Auger, ISS, and even EMP, compared surface compositions with compositions at depths up to 1000 A and bulk compositions and showed conclusively that many elements are concentrated on the surface of particles of coal a This has been shown also more indirectly by analyzing various particle size fraction of samples. Linton further concluded that since coal ash is predominantly made up of an insoluble aluminum silicate glass the analysis obtained by a water or dimethyl sulfoxide extraction might be more meaningful in terms of health effects than bulk composition analyses. Craig, et al.,[69] used ESCA to examine the chemical states of sulfur in ambient pollutants and found seven species--SO_3, $SO_3^=$, $SO_4^=$, SO_2, S°, and two kinds of sulfides. Several workers cross-compared ESCA results with wet chemical and other methods and found variations of a factor of 2, with much higher discrepancies on volatile species.

As stated earlier, many problems are encountered in the application of ESCA to pollutant analyses. These include poor resolution of peaks

resulting from different elements in the same oxidation state; poor quantitative data even with the use of standards; requirement for a hard vacuum which with localized heating from X-ray bombardment can result in loss of NH_4NO_3, HNO_3, H_2SO_4 acid species, and others; difficulty in suitably mounting samples, and of course the problem that ESCA is a surface technique method which makes data interpretation more difficult. However, since ESCA is a surface analysis technique (and this is advantageous in many respects) it is difficult to standardize and to intercompare results with those obtained by other methods. The complexity and heterogeneity of pollutant particles enhances the difficulties of carrying out ESCA analyses. Certain elements or species are present on the surface of fly ash along with carbon. Others such as iron compounds are bulk components. Ion etching can be used to look beyond a particle surface, but this can further increase the difficulty of interpretation. Much more work needs to be done in looking between ESCA results and results from other methods before ESCA can be used routinely in compound identification. Certainly the combination of ESCA and Auger instrumentation (electron excitation) can provide considerable data on surface species.

The general conclusion is that ESCA provides considerable insight into compound species present in pollutant particulates and especially in respect to surface composition, but correct interpretation of data quantitatively is difficult. This, coupled with problems of "presenting" the sample and maintaining its integrity in the X-ray or electron beam, makes ESCA or ESCA augmented by Auger still a development technique. In substance, this abbreviated conclusion is apparently that obtained also by C. H. Lockmuller[79] who recently evaluated ESCA and other techniques for their applications to inorganic compound characterizations of emission species and by McAlister[80] of the NBS laboratories who evaluated ESCA similarly for characterization of St. Louis particulate matter.

ISS (ion scattering spectrometry), SIMS (secondary ion mass spectrometry) also are surface analysis techniques and suffer many of the disadvantages of ESCA. Much more work needs to be carried out by the use of standards and intercomparisons of results before ISS or SIMS ever approach routine use in pollutant analyses.

Chemical Phase

Chemical phase analysis as defined by Steger in a review article[81] is the determination, by a chemical dissolution technique, of the distribution of an element in an ore or rock with a goal of selective dissolution of one or more minerals present. Since fly ash particulates do not contain natural minerals, the techniques and uses of chemical phases analyses usually must be modified from those given in the literature. However, since the goal remains essentially the same, it appears useful to retain, and use of the term "chemical phase analysis" for work on particulate pollutants which involve valence determinations and other selective dissolution techniques which lead toward identifying the presence and chemical states of elements and elemental groupings. Possibly because of the lesser availability of sophisticated instrumentation, chemical phase analysis is utilized most by the eastern

European and U.S.S.R. countries, and this introduces difficulties because translations are not readily available and access to the original work is difficult.

Below are examples of chemical phase or preferential and controlled chemical state determination of species in particulate samples. Many other similar techniques can be found and are adaptable for identification of other species or chemical states.

Free H_2SO_4 acid determination has received considerable attention in atmospheric aerosol analysis as well as fossil fuel emission, but the various methodologies proposed still have not been totally adequate nor statisfactory. Leahy, et al.,[82] state that H_2SO_4 acid can be extracted and determined without interferences from other sulfate salts using a benzaldehyde extraction. Barton and McAdie[83] have described an isopropanol extraction method which they found unique for H_2SO_4. Others, including Shafer[84], Scaringelli[85], and West[86], described methods for sulfuric acid aerosols in the presence of other sulfate salts. Estimates of 10 percent for ambient to 65 percent for oil fly ash are given for the relative proportion of sulfuric aerosol to the total sulfate content.

Vanadium, a key pollutant found in high concentrations in oil-fired power plant fly ash emissions using South American crudes, can be present in several chemical combinations. Knowledge of the valence state(s) of vanadium can be useful in determining its chemical form. Vanadium (V^{V} and V^{IV}) have been determined in the presence of each other by Shcherbakova, et al.[87] Working with catalyst samples they found optimal conditions for the sequential determination of V^{V} and V^{IV} by use of an extraction-photometric method. Rao[88] has described a potentiometric titration for determining V^{III} alone and in mixture with V^{IV}.

The several forms of carbon present in aerosols have been determined by several means: Grosjean[89] used a solvent extraction followed by organic carbon analyzer analysis. Appel, et al.,[90] also working with atmospheric samples, developed a technique for estimating elementary carbon, and primary and secondary organics, while Mueller, et al.,[91] measured the carbonate-noncarbonate content of particulates. In our own work, XRD has shown carbon in oil fly ash to be largely amorphous but with some graphitic structure. Low concentration of $CO_3^{=}$ in fly ash and ambient particulate amples have been analyzed by us using a gas chromatographic technique.

Sant and Brasant[92] after a brief review of 21 methods for determining various forms of iron in mixtures, outline a simple and rapid method of sequential determination of Fe°, Fe^{++}, and Fe^{+++}. The sample is treated with brominol and filtered. Iron in the filtrate is titrated iodometrically. The oxide residue is dissolved with HCl under a CO_2 blanket with the Fe^{++} formed, equivalent to the FeO present, titrated with a standard vanadate solution, and the total Fe($\equiv$ FeO + Fe_2O_3) in the titrated solution is then obtained iodometrically. Brimblecombe and Spedding[93] in their studies of iron dissolution from pulverized fuel ash showed that the iron more likely is present as finites. This is in agreement with Minnick[23] who found that

a large fraction of the iron in pulverized fuel ash residues is nonmagnetic particles. If the iron were present as Fe_3O_4 a larger magnetic fraction would be expected.

Hexavalent chromium Cr^{VI} can be determined in the presence of iron, copper, nickel, and vanadium by the very sensitive s-diphenylcarbazide method.[94]

Young[95] has shown that CaO can be differentiated from many other calcium salts by its formation with a sucrose solution, a water-soluble saccharate. This can be titrated with a standard oxalic acid solution. Large quantities of the carbonate and oxide of magnesium have no effect on the determination of CaO by the procedures.

Components of fossil fuel fly ash emissions can be separated and determined by selective chemical means--e.g., the glassy constituents of coal ashes have been quantitatively determined by extraction with cold 40 percent HF acid as developed by Konopicky and Köhler[96]. Free silica in environmental samples has been determined by XRD, IR, and chemical means. These have been reviewed in detail by Anderson.[97] Free silica is a component of the crystalline phases present in many coal fly ash samples.

X-Ray Fluorescence

X-ray fluorescence (XRF) has been used indirectly in compound identification efforts to provide data on samples before and after chemical and/or physical separation--e.g., analyses before and after water leach can be used to identify soluble and insoluble species. In these applications the very good reproducibility and rapid multielement capabilities of XRF make the technique ideal for complex sample types such as fly ashes. Because of the non-destructive nature of excitation, the XRF equipment can be automated and computerized to provide accurate multielement data rapidly. Wagman, Bennett, and Knapp describe this application of XRF to particulate pollutants.[98,99] XRF also has been used to identify the chemical forms of elements in the atomic number range of 11 to 17 - Na to Cl. Gilfrich, Pickerar and Birks[100] have used a conventional single-crystal XRF analyzer to measure K_β emission of sulfur to quantitatively discriminate sulfate and sulfide forms. These authors project that similar identities can be obtained on P and Cl. The K_β X-ray emission results from the transition of valence electrons (from the M shell) to fill vacancies in the K shell and as such displays structure associated with the chemical combination of the element. Other workers[101,102] have used X-ray analyses to determine the valancies of vanadium and manganese and Paris[103] applied the technique to the direct determination of organic sulfur in coal.

EXPERIMENTAL

The experimental efforts were directed toward the investigation and application of well-established techniques since at the start of this program very little information was found available on even the compositions of oil-fired fly ash emissions. More recently, studies by EPA workers, Knapp, Bennett, and Conner(104,105,106) have been useful in filling this information gap. An exception to this technique selection process was the exploration and use of FT-IR which hitherto had been applied mostly to organic identification work.

FIELD SAMPLE COLLECTIONS

Samples of oil-fired and coal-fired fly ashes were collected from several power plant sites which burn fossil fuels of various origins with the objective of obtaining a range of fly ash sample compositions representative of present power production processes. Sampling was performed at the port holes in the stacks or ducts beyond any emission control process operation. The fly ash samples were obtained by simply inserting a 2-cm-diameter glass-lined probe into the center of the stack perpendicular to the stack stream flow and, with a 1 hp blower, drawing a portion of the flow into a fine mesh Teflon bag. A 24-hour sampling time period usually provided 50 to 75 grams of stack emission particulates. At the conclusion of the sampling period the Teflon bag was removed from the Hi-Vol container, sealed in a polyethylene bag, and returned to the laboratory for analyses of the collected particulates.

Sample pretreatment was considered carefully in carrying out the analyses of fossil fuel particulate emissions samples since unknown alterations of their chemical forms must be avoided. Samples collected in the way described from stack exit flues at temperatures of about 150 C contain large amounts of water, and pretreatments such as desiccation and heating can alter the sample weights and chemical forms. From the structural, crystallographic and/or optical--XRD, IR, petrography--analytical aspects, it is desirable to work with samples in a stable, moisture-free condition since the presence of loose and even bound forms of water, "nonessential and essential" hydrogen, complex the identification efforts. The practice of drying samples at 105 C before bottling, weighing, and analysis is not applicable to the wet particulate emissions since for many samples there is no point where loose, unbound, capillary water only is removed by heating in air atmosphere. This is illustrated by the data given in Table 9 for samples collected at the stack exit ports of coal and oil-fired power plants. Thermograms of a composite of four oil fly ash samples (equal amounts of each mixed together) heated slowly at 1 degree per minute in air and in argon are shown in Figure 1. The thermogram for the oil-fired fly ash composite heated in air shows a cont nuous weight loss over a 15 hour

TABLE 9. WEIGHT LOSSES OF FLY ASH SAMPLES ON SLOW HEATING IN AIR (IN PERCENT)

	105 C	200 C	400 C	750 C
Oil Fly Ash 1	2.4	4.5	18.0	22.5
Oil Fly Ash 2	3.0	4.8	69.5	74.0
Oil Fly Ash 4	4.5	12.5	28.0	57.0
Oil Fly Ash 5	5.05	10.6	36.9	45.5
Coal Fly Ash NBS	0.25	0.55	1.1	4.1
Coal Fly Ash 1	1.0	1.8	2.6	4.7
Coal Fly Ash 2	4.0	5.4	13.0	19.2
Coal Fly Ash 3	4.0	6.5	9.0	24.2

heating increase at a 1 C per minute change. The sequence of weight losses, as shown by individual sample TGA and DTA plots in air, indicate capillary or unbound water, hydrated or bound water, carbon, and then partial $SO_4^=$ losses. The partial and variable losses of $SO_4^=$ are confirmed by the data given in Table 10 for $SO_4^=$ contents of samples before and after ignition at 750 C.

Thermograms based on heating the samples under argon show minor incremental weight changes between 200 and 400 C, as illustrated by the composite sample in Figure 1, indicating probable loss of most unbound water contents. IR and XRD spectral and pattern images obtained on the samples after heating under argon are much improved as are the microscopic appearances of viewed sample particle fields. Based on these findings, heating the samples under argon appears to be a reasonably satisfactory mode of removing the unbound water without altering otherwise the integrity of the sample structure, and based on individual thermograms for several samples, heating samples at 300 C under argon was adapted as the general preparation mode for IR, XRD, and microscopic examinations.

Sample Descriptions

Six oil-fired and five coal-fired fly ash samples were obtained for the methodology development work. These are:

Oil Fly Ash No.1--

This is an aged sample obtained during a 1973 research program from a Connecticut power plant purportedly burning No.6 fuel oil of a domestic origin. No sample of the fuel oil was available for analysis. As judged by the particle size range of the fly ash, the ESP control probably

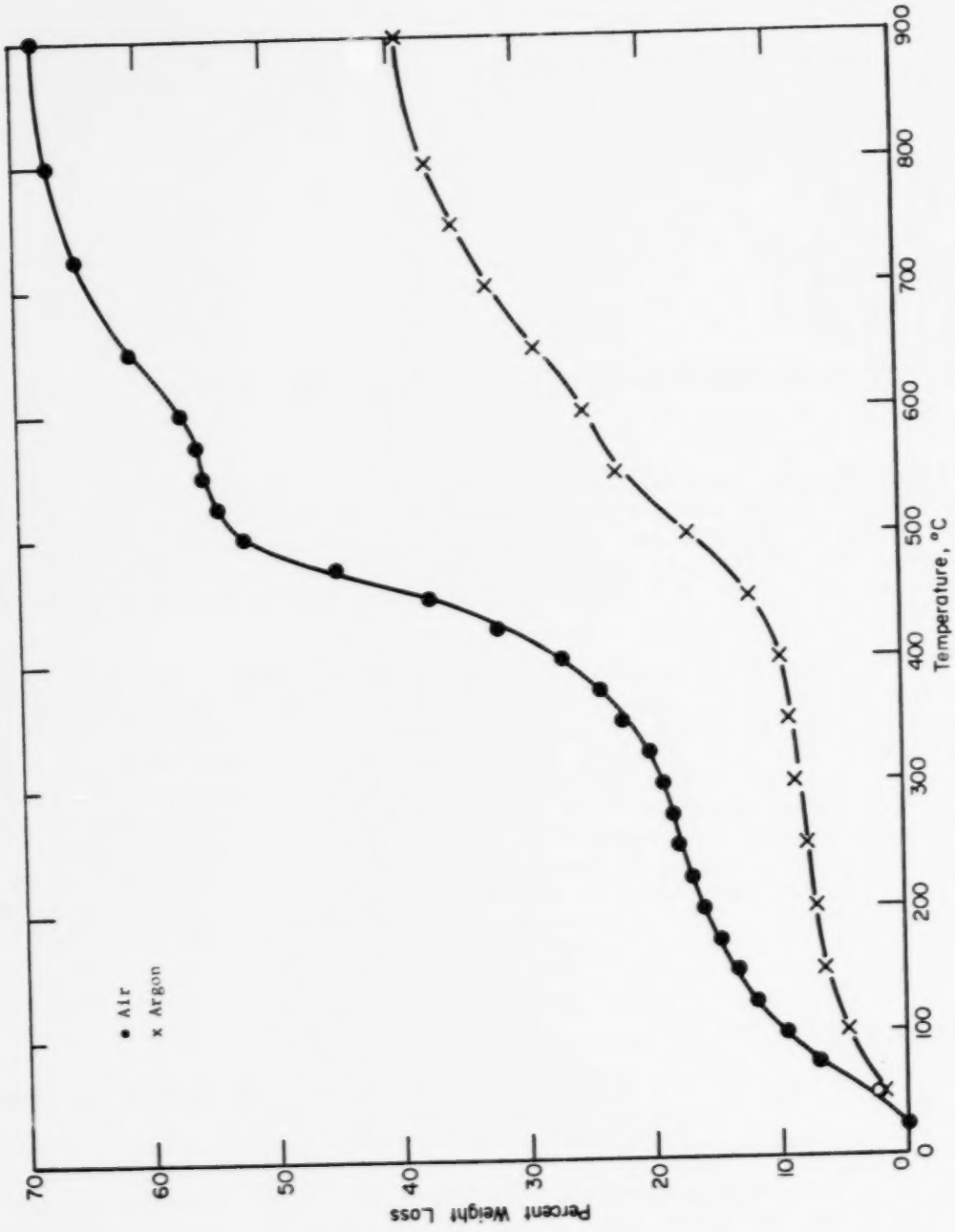

FIGURE 1. THERMOGRAMS OF OIL-FIRED FLY ASH COMPOSITE SAMPLES IN AIR AND ARGON - 1°C/MINUTE

TABLE 10. CHANGES IN $SO_4^=$ CONTENTS OF FLY ASH SAMPLES BEFORE AND AFTER IGNITION IN AIR AT 750 C (RESULTS IN PERCENT)

	Total $SO_4^=$ In Collected Samples	$SO_4^=$ After Ignition	Loss of $SO_4^=$ at 750 C
Oil Fly Ash 1	36.9	28.7	-8.2
Oil Fly Ash 2	12.0	10.4	-1.6
Oil Fly Ash 4	41.2	21.0	-20.2
Oil Fly Ash 5	57.6	18.9	-38.7
Coal Fly Ash NBS	0.98	0.20	-0.78
Coal Fly Ash 1	5.0	3.0	-2.0
Coal Fly Ash 2	7.26	0.92	-6.34
Coal Fly Ash 3	22.0	0.90	-21.1

was not operating at the time of sampling, and as evidenced by the high concentration of magnesium in the collected fly ash, a magnesium additive was added to the fuel. The high $SO_4^=$ value casts some doubt on the oil being of domestic origin.

Oil Fly Ash No.2--

The No.2 oil fly ash sample was collected from a Florida utility boiler which at the time of collection was burning a No.6 fuel oil derived from a Venezuelan crude. Front-end magnesium additive was employed in the combustion process. At the time of sampling, the plant was operated at a minimal excess air. Analyses of the fuel oil and additives are given in Table 11.

Oil Fly Ash No.3--

This sample was collected at the same location as the No.2 sample with the sampler being allowed to operate unattended for about a week. During that period the collected particulates became excessively wet-- 36 percent free water. Compositionally the collected sample, on a dry basis, was similar to the No.2 above.

Oil Fly Ash No.4--

This sample was collected from a South Carolina electric utility boiler. At the time of sampling the plant was burning a No.6 fuel oil derived from predominantly Venezuelan crude origin. Both a front-end (Chesco 22) and a back-end additive (Coaltrol) were being used and the plant was operating at a normal air-to-fuel combustion ratio. Analyses of the additives and the fuel oil are given in Tables 12 and 13.

TABLE 11. ANALYSES OF FUEL OIL AND ADDITIVES USED DURING COLLECTION OF NO.2 OIL-FIRED FLY ASH - RESULTS IN PPM EXCEPT WHERE PERCENT IS GIVEN

	Fuel Oil (No Additive)	Fuel Oil (With Additive)	Mg Additive No. 1	Mg Additive No. 2
Mg	9	137	25.8%	33.5%
V	570	540	<5	<5
Ni	72	69	<5	<5
Fe	5	5	500	2000
S	2.5%	2.47%	--	--
Al	1	2	2%	0.2%
Si	2	5	500	0.4%
Ca	5	10	0.2%	1%
Mn	1	1	50	2000
Pb	1	1	2000	<5
Ash	0.11%	0.18%	52%	59.7%
Na	20	20	--	--
K	3	4	--	--

TABLE 12. SEMIQUANTITATIVE ANALYSES OF ADDITIVES USED DURING COLLECTION OF NO.4 OIL-FIRED FLY ASH*

Element	Front-End Additive	Back-End Additive	Element	Front-End Additive	Back-End Additive
Mg	15	30	Fe	0.03	0.2
Ca	0.2	0.3	Pb	0.1	--
Si	<0.05	2	B	0.01	0.04
Al	2	0.3	V	<0.01	<0.01
Na	0.05	3	Ash	33.4	93
K	<0.05	0.5			

*Results in percent.

TABLE 13. ANALYSES OF FUEL OILS USED DURING COLLECTION OF NO.4 OIL-FIRED FLY ASH*

Element	No.6 Fuel Oil (12/14/76)	No.6 Fuel Oil (12/15/76)	No.6 Fuel Oil (12/16/76)
Ash	0.10%	0.09%	0.095%
S	2.15%	2.2%	2.1%
Na	10	10	10
K	4	4	4
Mg	6	7	5
V	446	450	445
Ni	62	60	64
Fe	45	45	45
Al	2	2	2
Si	3	3	3
Ca	5	5	5
Mn	<1	<1	<1
Pb	<1	<1	<1

*Results in ppm except where percent is given.

Oil Fly Ash No.5--

This fly ash was taken at the same site as was the No.2 sample but about 6 months later. Reportedly the plant had switched to a fuel oil derived from a Near East crude. The analysis of the fuel oil combusted during the sampling period, given in Table 14, is lower in vanadium content.

TABLE 14. ANALYSIS OF FUEL OIL USED DURING COLLECTION OF NO.5 OIL-FIRED FLY ASH

Element	No.5 Oil-Fired Fly Ash (2/10/77)
Mg	114
V	292
Ni	50
Fe	17
S	2.65%
Al	1
Si	4
Ca	7
Na	159
K	7
Mn	1
Pb	<1
Ash at 550 C	0.14%

*Results in ppm except where percent is given.

Oil Fly Ash No.6--

This sample was obtained from a Louisiana electric utility plant allegedly burning a domestic derived fuel oil. Two additives were available for combustion control. However, based on analysis of the collected ash, the Mn additive was not used during the sampling period. The analyses of the fuel oil and additives are given in Table 15.

TABLE 15. ANALYSIS OF FUEL OIL USED DURING COLLECTION OF THE NO.6 OIL FIRED FLY ASH SAMPLE AND ADDITIVE COMPOSITIONS

	Fuel	Apollo MC-7 Additive	Betz FS-62U Additive
Mg	1490	5000	25%
V	40	100	--
Ni	20	400	--
Fe	15	2%	100
S	1.56%	--	--
Al	60	5%	20%
Si	10	3%	2000
Ca	5	4000	5000
Na	8	--	--
K	6	--	--
Mn	<1	35%	--
Pb	<1	--	--
Ash at 550 C	0.5%	53%	56.5%

NBS Coal Ash--

This is the NBS Standard Reference Material 1633 which, according to the certificate, is a blend of six ashes - five of which were collected by electrostatic precipitators and one by a mechanical collector. These were sieved and the portion passing through a 170 mesh sieve were taken and blended to make up the SRM.

Coal Fly Ash No.1--

This is an aged sample collected in 1973 at an electric utility plant operating in West Virginia. The sample was collected from the stack, past the ESP. No coal fuel was available for analysis.

Coal Fly Ash No.2 and No.3--

The No.2 and No. 3 coal-fired fly ash samples were collected in July, 1977, at an Ohio and a Kentucky power plant, respectively. The operating capabilities of these power plants are between 100 to 200 megawatts and both use ESP controls in burning Ohio and Appalachian origin pulverized coals of compositions given in Table 16.

TABLE 16. ANALYSES OF COAL FUELS USED DURING COLLECTION OF NOS. 2, 3, 4, AND 5 FLY ASH EMISSION SAMPLES(a)

	Coal Fuel No. 2	Coal Fuel No. 3	Coal Fuel No. 4	Coal Fuel No. 5
S	3.87	3.62	5.14	0.49
Fe	1.0	0.9	2.0	--
Al	1.3	1.0	2.0	--
Si	1.0	1.7	3.0	--
Ca	0.2	0.3	1.5	--
Mg	0.02	0.1	0.2	--
Ti	0.02	0.1	0.1	--
Ash at 700 C	8.2	14.4	27.7	7.03
Zn	<0.1	<0.1	0.30	0.03

(a) Results in percent.

Coal Fly Ash No. 4. This sample was collected in May, 1978, from a utility power plant (rated at 875 megawatt capacity) burning a locally mined subbituminous coal fuel of a composition given in Table 16. The control mechanism is a wet-lime scrubber process. The combination of a high-ash, high-sulfur fuel with scrubber control resulted in a fly ash of considerably different composition than other coal-fired fly ashes--see Table 17. The most striking differences are the considerable water-solubility of the ash and high concentrations of $SO_4^{=}$ and heavy metal compounds. The latter appeared to be derived from a zinc-base mineral present in the coal. The plume has a high visibility with particulate emissions estimated at 0.213 lb/10^6 Btu.

Coal Fly Ash No. 5. This sample was collected in May, 1978, at a utility power plant (rated at 800 megawatts) burning a low ash, low sulfur Wyoming coal of a composition given in Table 16. The emission control used is an electrostatic precipitator. At a short distance the plume is barely visible. Particulate emissions have been measured at 0.012 lb/Btu.

These samples appear to be sufficiently representative of fly ashes emitted from oil and coal-fired utilities which use fuels of various origins and control processes to test the efficiencies of developed compound methodologies thoroughly. The effects of rapid "aging" or changes in sample composition during and subsequent to sample collection were not studied in this program, although it is believed that these effects can be of considerable significance.

ANALYTICAL METHODOLOGY FOR ELEMENT CONTENT OF FOSSIL FUEL PARTICULATE EMISSIONS

Prior to inorganic compound identification, determinations were made of the elemental contents of the samples, both as a guide to the

selection and use of the inorganic compound techniques and quantification and substantiation of the compound results obtained. The techniques used are only briefly outlined below since they are well established and thorough discussions on their applicability to fuel and fuel ashes are given in numerous publications including references 107 to 110.

Atomic Absorption Spectrometry (AAS)

AAS is used for determining the metallic elements present in concentrations<0.01 percent in the samples with the exception of the determinations of Si and Al in the coal-fired fly ashes. Elements of key interest such as As, Se, Hg, Pb, Tl, and others also are determined by AAS at concentrational levels down to about 0.001 percent when it is desired to obtain better quantitative data than obtained by SSMS.

Equipment: Perkin-Elmer 305B with HGA 2000 high temperature graphite furnace and deuterium accessories.

Spark Source Mass Spectrography (SSMS)

Samples are mixed with high purity graphite to yield a 40 percent graphite mixture and pressed into 7/64-inch-diameter by 5/16-inch conductive electrodes. The sample electrodes are placed into the ion source and a series of graded exposures are recorded on a photoplace with the heaviest exposure providing sensitivities of 0.1 ppm, atomic basis. The photo plates are interpreted visually using sensitivity factors derived from analyses of reference standards. SSM data is used for the semiquantitative estimation of concentrations of elements present in contents of < 0.1 percent in the samples.

Equipment: AEI MS-702 R using 2 x 12 inch Ilford Q2 Plates

Carbon, Hydrogen, Nitrogen

Three mg of sample are weighed into a preweighed platinum boat, reweighed, and combusted at ~950 C after a purge cycle with oxygen to remove air. The instrument automatically controls the purge cycle, a helium sweep cycle and the read-out cycle. C, H, and N contents are measured as CO_2, H_2O, and N_2 by thermal conductivity cells. The instrument is calibrated by extensive use of standards.

Equipment: Perkin-Elmer Model 240 Elemental Analyzer
LECO Carbon-Oxygen Determinator

Ion Chromatography -- Cl^-, F^-, NO_3^-, $SO_4^=$ Determinations

Typically a 1-ml portion of sample solution is introduced into an ion exchange column containing a low-capacity resin, eluted with a weak $NaHCO_3$-$NaCO_3$ solution and the anions are separated. The effluent stream is passed through a second ion exchange column (a suppression column) to remove

unwanted ions and then through a conductivity cell where the concentrations of the separated anions are read as a series of peaks on a strip chart recorder. Calibration is achieved by processing standard solutions similarly. The ion chromatograph has seven electronic attenuations which allow coverage of seven concentrational ranges from about 0.5 to 1000 ppm of the sample solution.

Equipment: Dionex Ion Chromatography

Nitrite (NO_2^-) Determination

Colorimetric method through formation of azo dye formed by coupling diazotized sulfanilic acid with N-(1-naphthyl)-ethylenediamine.

Sulfite ($SO_3^=$) Determination

Titration with standarized potassium iodide-iodate titrant releasing free iodine giving a blue color with starch indicator.

Total Sulfide (S) Determination

Acidify sample in sulfur evolution apparatus, heat while passing purging gas through system, collect any H_2S released by passing gas stream through ammoniacal zinc acetate solution, acidify, titrate with KI solution.

Ammonium (NH_4^+) Determination

Specific ion ammonia gas-sensing electrode.

Total Organics

Repetitive (5) methylene chloride extractions made on 0.5 g of sample and the extracted phase carefully dried and weighed to obtain the total organic mass content extracted.

Total Reduced Sulfur Species--
$S^=$, $SO_3^=$, $S_2O_3^=$

Treat samples with 0.1 N iodine solution, acidify and titrate unreacted iodine with 0.1 N sodium thiosulfate.

Fe, Al, Si in Coal Ashes

Fusion of ash with NaOH, leach with water, acidify with HCl and determination of Si as silico-molybdenum blue and aluminum as the calcium alizarin red-S complex. Decomposition of ash with HF, HNO_3, and H_2SO_4 acids. Fume off Si, dissolve residue in water, and spectrophotometric determination of Fe as tiron complex.

RESULTS OF COMPOSITION ANALYSES

The results obtained by use of the above techniques are given in Tables 17 and 18. Included in Table 17 are the concentrations of certain components on the bases of water solubility and insolubility--e.g., Oil Fly Ash No. 1 contains 36.9 percent $SO_4^=$ with 36.0 percent being water-soluble and 0.9 percent insoluble, etc. The data given in Table 17 show that a very large percentage of the oil-fired fly ash samples are water soluble as well as substantial percentages of certain coal-fired fly ash samples. These data also show $SO_4^=$ to be the only significant form of sulfur in the fossil fuel particulate emission samples. Although the method of determination of $SO_4^=$ might measure other sulfur forms, separate $S^=$ determinations and total reduced sulfur species determinations have shown the presence of other sulfur forms to be neglible. This has been confirmed by $SO_4^=$ determined values correlating closely with total sulfur values (determined by combus tion) calculated as $SO_4^=$. The $SO_4^=$ is nearly all in the water-soluble phase of the samples and is essentially the only anion present in this phase.

These findings suggest a ready, simple mode of fractionating fossil fuel particulate emissions into water-soluble metal (and ammonium) sulfates and water-insoluble metal oxides (and silicates) plus inert carbon. Any free H_2SO_4 acid of course also is contained in the water-soluble phase of the samples, but H_2SO_4 acid has not been found to be present in large percentages except in the No. 4 coal-fired fly ash which was collected at a port behind the wet scrubber control mechanism.

The separations or fractionations of the samples into water-soluble/insoluble phases has proved useful for structural identifications of specific metal sulfate forms, principally by FT-IR, and of oxide forms by XRD.

COMPOUND METHODOLOGY

Chemical Phase Methods and Separations

Free H_2SO_4 Acid--

A benzaldehyde extraction procedure was used similar to that described in several recent literature references. The method used basically followed the procedures described by Leahy, Tanner, et al.,[111,112] and Barrett, et al.[113] Both of these groups checked the specificity of benzaldehyde as an extractant for H_2SO_4 acid and the recovery of H_2SO_4 acid via spikes and/or generation of known quantities of H_2SO_4. Recoveries were found to be greater than 80 percent and experimental tests showed the extraction to be specific for H_2SO_4. However, the results obtained by us were very erratic showing reproducibility errors of a factor of 10, attributable at least in part to formation of benzoic acid.

The procedure used is as follows: Weigh 0.1 gram of sample into a graduated centrifuge tube. Extract into 3 ml of benzaldehyde (prepared fresh by reduced pressure distillation under dry nitrogen) and mix 5 to 10 minutes with a vortex stirrer, holding tube at 45 degree angle and rotating during the stirring. Centrifuge at ~850 rcf until sample is well packed into the bottom of the centrifuge tube. Transfer the benzaldehyde into a

TABLE 17. OIL AND COAL FIRED FLY ASH COMPOSITIONS - MAJOR CONSTITUENTS (PERCENT)

		C	H	N	NO_3^-	NO_2^-	NH_4^+	$SO_4^=$	$SO_3^=$	S	Cl	P	Si
Oil-Fired Fly Ashes													
No. 1	Total Sample Content	12.4	0.9	0.1	0.005	<0.01	0.012	36.9	<0.01	<0.01	0.05	0.008	0.31
	Water-Soluble Content							36.0	<0.01	<0.01			0.01
	Water-Insoluble Content							0.9	<0.01	<0.01			0.31
No. 2	Total Sample Content	69.0	0.7	0.9	0.013	0.005	0.13	12.0	<0.01	<0.01	0.02	0.002	0.2
	Water-Soluble Content							12.0	<0.01	<0.01			0.01
	Water-Insoluble Content							0.15	<0.01	<0.01			0.2
No. 4	Total Sample Content	21.5	1.0	0.9	0.02	0.01	0.81	41.2	<0.01	<0.01	0.02	0.004	0.2
	Water-Soluble Content							41.1	<0.01	<0.01			0.01
	Water-Insoluble Content							0.1	<0.01	<0.01			0.2
No. 5	Total Sample Content	1.5	1.2	0.1	0.02	<0.01	0.16	57.6	<0.01	<0.01	0.05	0.001	0.05
	Water-Soluble Content							58.6	<0.01	<0.01			0.01
	Water-Insoluble Content							0	<0.01	<0.01			0.05
No. 6	Total Sample Content	14.5	2.4	6.5	<0.01	0.03	7.3	49.2	<0.01	<0.01	0.06	0.05	0.22
	Water Soluble Content							48.4	<0.01	<0.01			0.01
	Water-Insoluble Content							0.8	<0.01	<0.01			0.22
Coal-Fired Fly Ashes													
NBS	SRM 1633 Total Sample	3.3	0.1	<0.1	<0.01	<0.01	<0.01	0.98	<0.01	<0.01	0.005	0.12	20.9
	Water Soluble Content							0.60	<0.01	<0.01			
	Water-Insoluble Content												
No. 1	Total Sample Content	1.7	0.3	<0.1	<0.01	<0.01	<0.01	3.05	<0.01	<0.01	<0.003	0.14	19.7
	Water Soluble Content							2.13	<0.01	<0.01			
	Water Insoluble Content												
No. 2	Total Sample Content	7.0	0.5	0.1	<0.01	<0.01	0.06	6.9	<0.01	<0.01	0.007	0.02	16.7
	Water Soluble Content							5.75	<0.01	<0.01			
	Water Insoluble Content												
No. 3	Total Sample Content	0.5	0.7	<0.1	0.02	<0.01	0.01	22.1	<0.01	<0.01	0.05	0.08	16.6
	Water Soluble Content							19.6	<0.01	<0.01			
	Water Insoluble Content												
No. 4	Total Sample Content	0.1	1.2	<0.1	0.03	<0.01	0.15	50.6	<0.01	<0.01	0.06	0.2	6.2
	Water Soluble Content							50.2	<0.01	<0.01			<0.01
	Water Insoluble Content												6.2
No. 5	Total Sample Content	0.1	<0.1	<0.1	<0.01	<0.01	0.01	5.23	<0.01	<0.01	<0.01	0.05	10.8
	Water Soluble Content							2.32	<0.01	<0.01			
	Water Insoluble Content												

TABLE 17. (CONTINUED)

		Al	Fe	Ni	V	Mg	Ca	Na	K	Total Organics	Water Solubility	H_2O	H_2SO_4	pH
Oil-Fired Fly Ashes														
No. 1	Total Sample Content	1.25	0.61	1.66	2.27	18.4	1.0	3.91	0.13	<0.1	58.0	7.0	<0.1	3.9
	Water Soluble Content	0.5	0.30	1.0	0.50	4.71	0.6	3.9	0.13					
	Water Insoluble Content	0.75	0.31	0.66	1.77	13.7	0.4	0.01	0					
No. 2	Total Sample Content	0.05	0.40	0.85	6.68	3.41	0.31	0.30	0.1		23.3	5.0	0.2	2.7
	Water Soluble Content	0.02	0.25	0.60	2.23	1.15	0.15	0.30	0.1					
	Water Insoluble Content	0.03	0.15	0.25	4.45	2.26	0.16	0	0					
No. 4	Total Sample Content	0.40	0.41	1.29	10.2	5.94	0.1	0.50	0.19	0.053	72.0	4.5	0.04	2.42
	Water Soluble Content	0.23	0.20	1.06	8.98	5.0	0.07	0.51	0.12					
	Water Insoluble Content	0.17	0.21	0.23	1.22	0.94	0.03	0	0					
No. 5	Total Sample Content	0.01	0.48	2.28	12.85	2.50	0.20	2.02	0.10	<0.1	98.5	5.5	1.0	2.15
	Water Soluble Content	<0.01	0.49	2.31	12.9	2.65	0.19	2.0	0.09					
	Water Insoluble Content	0.01	0	0	0	0	0.01	0	0					
No. 6	Total Sample Content	1.42	0.40	0.35	1.10	2.4	0.32	0.20	0.12	0.1	83.0	2.1	1.5	2.22
	Water Soluble Content	0.27	0.43	0.30	0.78	2.4	0.16	0.21	0.11					
	Water Insoluble Content	1.15	0	0.05	0.32	0	0.16	0	0					
Coal-Fired Fly Ashes														
NBS	SRM 1633 Total Sample	12.7	6.5	0.01	0.02	2.0	4.2	0.30	1.75	<0.1	3.5	0.03	<0.1	11.35
	Water Soluble Content													
	Water Insoluble Content													
No. 1	Total Sample Content	11.3	12.6	0.06	0.02	0.52	1.5	0.60	1.54	0.04	5.3	1.0	<0.1	4.5
	Water Soluble Content													
	Water Insoluble Content													
No. 2	Total Sample Content	10.9	14.1	0.02	0.03	0.2	0.40	0.05	1.0	0.072	13.0	4.0	2.0	3.17
	Water Soluble Content	0.63	0.56	0.01	0.01	0.01	0.18	0.03	0.5					
	Water Insoluble Content	10.27	13.54	0.01	0.02	0.01	0.22	0.02	0.5					
No. 3	Total Sample Content	8.79	7.90	0.05	0.05	0.5	3.0	0.08	1.1	0.11	34.0	5.0	2.1	2.73
	Water Soluble Content	1.63	1.94	0.04	0.04	0.2	1.8	0.06	0.6					
	Water Insoluble Content	7.16	5.96	0.02	0.02	0.4	1.2	0.02	0.5					
No. 4	Total Sample Content	1.2	7.56	0.02	0.03	0.3	2.65	0.1	1.0	<0.1	79.2	3.9	16.5	2.2
	Water Soluble Content	0.6	6.55	0.02	0.02	0.3	2.6	0.1	0.4					
	Water Insoluble Content	0.6	1.0		0.01	0	0.05	0	0.6					
No. 5	Total Sample Content	13.0	3.64	0.05	0.04	2.0	21.3	1.0	1.0	<0.1	9.1	1.0	0.1	11.3
	Water Soluble Content	0.4	0.02	0.01	<0.01	0.01	1.0	<0.1	<0.1					
	Water Insoluble Content	12.6	3.6	0.04	0.03	2.0	20.3	1.0	1.0					

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TABLE 18. OIL AND COAL-FIRED FLY ASH COMPOSITIONS - TRACE CONSTITUENTS

Element	Oil-Fired Fly Ashes					Coal-Fired Fly Ashes					
	No. 1	No. 2	No. 4	No. 5	No. 6	NBS	No. 1	No. 2	No. 3	No. 4	No. 5
Li	0.5	0.5	0.2	3	100	300	0.1	200.	200.	150.	20.
Be	<.05	0.3	0.2	0.3	0.1	5.	0.5	1.5	1.5	1.	10.
B	30.	0.5	5	3.	1	100.	100.	300.	200.	200.	400.
F	4	<1	3.	5.	<1.	10.	20.	30.	50.	200.	20.
Sc	9	<1	5.	3.	<1	20.	10.	30.	40.	10.	50.
Ti	5.0	300	400	400	700	6000.	2000.	100.	3000.	3000.	7000.
Cr	100	50	1000	500	450	130.	100.	150.	1000.	400.	200.
Mn	200	200	200	500.	300	500.	50.	300.	200.	100.	500.
Co	50	50	200	300.	300	50.	5.	70.	30.	15.	10.
Cu	50	100	200	400.	400	120.	30.	200	300.	400.	200.
Zn	40	40	200	400	200	200.	20.	800.	1200.	7.3*	300.
Ga	5	5	50	60	40	50.	10.	100.	60.	6.	5.
Ge	10.	1	10	10.	7.	20.	10.	70.	70.	100.	40.
As	35	20	30	30.	20.	60.	20.	100.	100.	2000.	30.
Se	2	5	10	3.	7.	10.	5.	20.	20.	40.	5.
Br	10	3	25	25.	2.	10.	15.	5.	20.	25.	10.
Rb	5	1	5	4.	7.	150.	5.	400.	700.	60.	200.
Sr	500	100	300	300.	200.	1500.	2000.	200.	150.	200.	3000.
Y	50	3	5	10.	10.	30.	50.	100.	30.	5.	100.
Zr	50	5	20	20.	10.	200.	100.	200.	50.	60.	200.
Nb	10.	2	1	1.	2.	7.	5.	10.	7.	5.	5.
Mo	100	50	100.	100.	150.	20.	10.	40.	70.	500.	70.
Ru	3	<1	<1	<1.	<1.	<0.5	<0.5	<0.5	<0.5	<1.	<1.
Rh	<3	<1	<1.	<1.	<1.	<0.5	<1.	<0.5	<0.5	<1.	<1.
Pd	1	<1	<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.
Ag	1.	<1	<1.	<1.	<1.	<0.5	<1.	0.7	0.7	<1.	<1.
Cd	1.	<1	<1.	<1.	<1.	15.	2.	8.	10.	20.	1.
In	<3	1.5	4	3.	4.	<0.5	<0.5	<0.5	<0.6	2200.	15.
Sn	<0.5	<0.5	<0.5	<0.5	<0.5	3.	3.	10.	10.	<1.	<1.
Sb	20	3.	5.	5.	3.	7.	1.	10.	10.	100.	15.
Te	<0.5	<0.5	<0.5	10.	150.	<0.5	<0.5	<0.5	15.	500.	15.
I	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	61.	10.
Cs	<1	<1	<2	3	1.	<0.5	1.	20.	40	<1.	<1
Ba	100	200	200.	1000.	1000.	10.	1000.	1000.	500.	20.	60.
La	45	10	50	50.	150	2500	40.	60.	80.	200.	3000.
Ce	50	5	25	30.	100.	70.	75.	100.	30.	20.	100.
59-71	120	15.	70.	60.	90	125.	40.	130.	60.	20.	100.
Hf	<0.5	<0.5	<0.5	<0.5	<0.5	90	3.	2.	2.	100.	250.
Ta	1	<1	<1	<1.	1.	10.	<1.	1.	1.	1.	10.
W	<1	<1	2.	2.	2.	2.	<1.	4.	4.	1.	3.
Re	<0.2	<0.2	<0.2	<0.2	<0.2	5.	<0.2	<0.2	<0.2	1.	7.
Ir	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<1.	<1.
Pt	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<1.	<1.
Au	0.3	0.3	<0.3	<0.3	<0.2	0.4	0.3	0.4	0.4	<1.	<1.
Hg	<0.5	<0.5	<0.5	<0.5	<0.4	<0.5	<0.5	<0.5	<0.5	<1.	<1.
Tl	<1	<1	<1.	<1.	<0.5	0.1	<1.	<1.	1.	<1.	<1.
Pb	300.	200.	400	400.	300.	2.	200.	15.	30.	30.	40.
Bi	<0.1	<0.1	<0.1	0.3	<0.1	80.	<0.1	150.	100.	7400.	70.
Th	10	5.	6.	4.	2.	0.7	10.	0.7	1.	<1.	2.
U	10.	5.	2.	10.	2.	20.	10.	40.	20.	20.	40.
						15.	10.	40.	30.	30.	50.

*Zn - 7.3% in total sample of which 6.9% is water soluble.

second graduated centrifuge tube, add 2 ml of deionized water and shake vigorously to extract the H_2SO_4 acid from the organic to the aqueous phase. Break up any resulting emulsion by centrifuging briefly at 850 rcf. Remove the aqueous layer by use of a water-wetted medicine dropper. Add 4 times the aqueous volume of isopropanol and a drop of 0.2 percent aqueous Thorin. Titrate with 0.01 N Ba^{++} (perchlorate) in the 1:4 H_2O: isopropanol mixture--one drop 0.01 N Ba^{++} solution = 5 µg H_2SO_4 acid.

Chemical-Physical Separations--

The chemical and physical complexities of particulates from fossil fuel sources make the task of identifying their chemical forms quite difficult. Generally, compound identification efforts can be simplified if the samples can be readily fractionated into a few separate phases without changing their chemical forms. Many of the available techniques for phase separation such as particle picking and/or use of the electron microprobe, scanning electron microscope, scanning transmission electron microscope or secondary ion mass spectrometer are useful but are too time consuming and tedious to be practical in examining in detail multiple samples for their quantitative inorganic compound identifies. Separation procedures based on density differences suffer because many of the fly ash particles are hollow spheres within spheres. Fractionations based on particle size are difficult to achieve because of particle agglomeration. Magnetic separation, applicable to coal fly ash samples, results only in enriching, but not completely separating, the magnetite phase of the samples.

The microscopic techniques do have merit, particularly in identifying trace metal associations with anion components, but many particles need to be deagglomerated and analyzed for their elemental concentration ratios and thus indirectly obtaining compound forms. This work is quite tedious whether performed by electron microprobe, scanning electron microscopy, secondary ion mass spectroscopy or scanning transmission electron microscope, and in fact only the latter technique has the capability of resolving very fine particles. However, since other compound identification techniques such as XRD and FT-IR cannot detect phases much below 0.5 percent, the STEM or other modes of microscopic examinations are needed for direct trace component compound identifications. Indirectly, compound types of trace metals may be deduced by performing spark source mass spectrogrpahic analyses on the total sample and on the sample after water extraction. The difference between the two values for a given element represents the soluble concentration. In fossil fuel fly ashes the principal soluble-phase anions is $SO_4^{=}$ and the principal insoluble phase anions are oxides and silicates.

Water Solubility Separation--

Separation on the basis of water solubility has been found to offer several advantages. The separation is readily achieved by simply stirring a 2-gram sample in 150 ml of water at room temperature for 1 hour by the use of a mechanical ("Mag-Mix") stirrer, filtering, washing, and drying the insoluble residue, and gently taking to dryness an aliquot of the soluble phase. After drying the insoluble residue is weighed to give the percent insoluble fraction and the percent soluble is obtained by difference. Based on experimental findings on the 12 fossil fuel-derived fly ashes given in Table 17 and other samples, the only anion of any significant concentration

in the soluble phase is the $SO_4^{=}$ and, in fact, the soluble phases contain nearly all of the $SO_4^{=}$ percent in the total unfractionated samples.

In the oil-fired fly ash work samples used in this program, the water-soluble phase represents from 66 to nearly 100 percent of the sample components exclusive of the inert, soot-like carbon. The soluble phase components of the oil fly ashes are primarily metal and NH_4^{+} sulfates plus any H_2SO_4 acid, while the insoluble phase components are carbon, oxides, and a minor amount of insoluble sulfates. The coal-fired fly ash samples also contain a water-soluble sulfate phase. These are much lower in concentrations due to the high percentages of insoluble iron-aluminum-calcium silicates and lesser amounts of insoluble cyrstalline minerals such as quartz, hematite, and magnetite in the coal fly ashes.

From the elemental analyses shown in Table 17 and 18, the data given in Table 19 for oil-fired fly ash samples were calculated basedon the assumptions that:

(1) The cation concentrations contained in the soluble fractions are sulfate forms since no other anions of any significant concentrations are present.

(2) The cation concentrations contained in the insoluble fractions are oxide forms primarily, plus limited concentrations of insoluble sulfates.

(3) The carbon of course is present as a water-insoluble component.

For example, considering the Mg in Sample No. 1, of the 18.1 percent present in the total sample, 4.71 percent is contained in the soluble phase and the remaining 13.7 percent in the insoluble phase. From the gravimetric factor for $Mg \rightarrow MgSO_4 \cdot H_2O$ of 5.69, the $MgSO_4 \cdot H_2O$ content would be

$$5.69 \times 4.71\% = 26.8\ MgSO_4 \cdot H_2O \quad .$$

Similarly, with the gravimetric factor for Mg MgO of 1.66 x 13.7%, the calculated insoluble MgO would be 22.8 percent.

These assumptions are not at odds with equilibrium thermodynamic calculations as discussed in a later section. As can be seen in Table 19, the possible calculated combinations total close to 100 percent for the No. 1 and No. 2 samples. The No. 5 combinations total only 95 percent, and the No. 6 total 91 percent. These are somewhat greater than the expected analytical accuracies and the discrepancies in these two samples are believed to be derived from inaccuracies in the sulfuric acid determinations and/or use of incorrect waters of hydration values. The total $SO_4^{=}$ contents of the compounds given at the bottom of Table 19 check reasonably well with determined concentrations given in Table 17 except for the No. 5 sample where the calculated SO_4 total 46.8 percent versus the determined value of 57.6 percent.

TABLE 19. POSSIBLE COMPOUND COMPOSITIONS OF OIL-FIRED FLY ASH SAMPLES BASED ON CHEMICAL ANALYSES OF SOLUBLE AND INSOLUBLE PHASES

Calculated Species	No.1	No.2	No.4	No.5	No.6
C as C	12.4	63.7	21.5	1.5	14.5
H_2O *	7.0	5.0	4.5	5.5	2.0
H_2SO_4*	0.1	0.2	0.05	1.0	1.5
NH_4 as $(NH_4)HSO_4$	0.08	0.83	5.18	1.03	46.6
Mg as MgO	22.8	3.8	1.6	0	0
Mg as $MgSO_4 \cdot H_2O$	26.8	6.6	28.5	14.8	13.6
V as V_2O_5	3.2	7.9	2.2	0	0.6
V as $VOSO_4 \cdot 3H_2O$	2.1	9.5	38.2	54.9	3.3
Fe as Fe_2O_3	0.45	0.2	0.3	0	0
Fe as $FeSO_4$	0.8	0.7	0.5	1.3	1.1
Ni as NiO	0.85	0.3	0.3	0	0.06
Ni as $NiSO_4$	2.65	1.6	2.8	6.0	0.8
Al as Al_2O_3	1.4	0.06	0.3	0.02	2.2
Al as $Al_2(SO_4)_3$	3.2	0.15	1.45	0	1.7
Si as SiO_2	0.55	0.4	0.45	0.05	0.5
Na as Na_2SO_4	12.1	0.95	1.55	6.25	0.6
K as K_2SO_4	0.3	0.2	0.2	0.2	0.25
Ca as CaO	0.55	0.2	0.04	0.01	0.2
Ca as $CaSO_4$	2.0	0.5	0.25	0.65	0.55
Other Elements as oxides/sulfates	1.3	0.35	0.75	1.0	1.0
Totals of above	100.7	103.2	110.6	95.2	91.1
Sulfates**	32.6	11.6	45.0	46.8	54.3

* H_2O and H_2SO_4 values are those determined as given in Table 16 rather than calculated values based on H.

** $SO_4^=$ contents of the calculated species.

These postulated chemical forms of inorganic compounds proved useful for both the XRD and subtractive FT-IR work in the interpretation work still in progress. MgO, V_2O_5, carbon and CaO patterns have been readily identified in the total sample, and, semiquantitatively, in the relative concentrations given in Table 19. $MgSO_4 \cdot H_2O$ and $VOSO_4 \cdot 3H_2O$ patterns have been identified in the total samples and in the soluble fractions (evaporated to dryness and baked under argon at 350 C) again in the approximate ratios given in Table 19. Interpretative searches are being continued to identify other compound forms with emphases being place on the oxides since it is known that the IR work may be more successful on the sulfate forms.

Chemical Valence of Vanadium--

In conjunction with the water solubility studies, it was noted that in several of the samples vanadium is present principally in a water-soluble form in the fly ash emissions. It was noted also that the water soluble solutions had a greenish to greenish-blue color proportional to the concentrations of vanadium determined present. Valence state measurements of vanadium in the oil fly ash samples were made with an adaption of an extraction-photometric method describes by Shcherbakova, et al.,[87] for the determinations of V^V and V^{IV} in vanadium catalyst samples. V^V was determined in the presence of V^{IV} at an acidity of 0.2 N since it was determined that at pH $\geq$ 1 vanadium (IV) is oxidized to vanadium (V) by atmospheric oxygen.

Following the procedure described by Shcherbakova, et al., 0.1 gram of oil fly ash sample was dissolved in 10 ml of 0.2 N HCl, the insoluble portion was filtered and washed with 0.2 N HCl and diluted to a volume of 100 ml. Extraction was carried out on a 2 ml aliquot using 5 ml of 10^{-2} PMBP solution (1-phenyl-3 methyl-4 benzoylpyrazolone-5), 1 ml pentanol, 4 ml chloroform and 8 ml 0.2 N HCl. V^V in the presence of any reduced vanadium was read spectrometrically at 500 NM. Total V in the sample was determined by oxidizing another aliquot of the above sample solution to V^V and repeating the extraction-photometric procedure. Reduced vanadium was found by the difference between the total vanadium determination result and the V^V value was determined in the presence of reduced vanadium. Total vanadium in the sample and in the water-soluble phase also were determined by atomic absorption analyses with better precision and accuracy than obtained by use of the extraction-photometric procedure.

The results obtained on the oil fly ash samples by use of the above methods are given in Table 20. As can be seen in the table, the reduced vanadium values (Column 6) coincide closely with total vanadium contents of the water-soluble fraction (Column 5). Since V^{II} and V^{III} vanadium states are very unstable, it is highly probable that the water-soluble vanadium is in the V^{IV} state.

The water solubilities of two reference vanadium compounds (ICN Pharmaceuticals vanadium sulfate and Alfa vanadium oxysulfate were compared with oil fly ash samples Nos. 2, 4, and 5 before and after heating under argon at 350 C. The vanadium sulfate was found to be very water insoluble both before and after heating. The $VOSO_4 \cdot 3H_2O$ was found to be highly water soluble before heating, exhibiting a deep greenish-blue color, but was only very slightly water soluble after heating. Anhydrous $VOSO_4$ is reported as insoluble in the literature. The oil fly ash samples behaved similarly with the unheated samples giving deep greenish coloration in the water solutions and the heated samples imparting no color. Semiquantitative analyses of the two reference vanadium compounds and fly ash samples showed no vanadium (<0.1%) was dissolved in water after the samples had been heated.

Based on the valence state determinations and the water solubility color tests, it appears that the oil fly ash samples contain water soluble $V^{IV}OSO_4 \cdot XH_2O$ and water insoluble V_2O_5, although there may be a possibility of a water soluble $V(SO_4)_2 \cdot XH_2O$ being present.

TABLE 20. V^V IN THE PRESENCE OF REDUCED VANADIUM AND TOTAL VANADIUM DETERMINATIONS (OIL-FIRED FLY AHS)[a]

Sample No.	Extraction-Photometric		Atomic Absorption		
	V^{V}[b]	V^{Total}[c]	V^{Total}	$V^{Water-Soluble}$	$V^{Reduced}$[d]
1	1.70	2.25	2.27	0.50	0.57
2	4.50	5.7	6.68	2.23	2.18
4	0.90	10.7	10.2	8.98	9.3
5	0.14	11.75	12.85	12.90	12.71
6	0.35	1.1	1.10	0.78	0.75

(a) Results in percent.

(b) V^V in presence of reduced vanadium.

(c) V^V after oxidation of reduced vanadium.

(d) Difference between Column 1 (V^V in presence of reduced vanadium) and Column 4 (total V determined by AAS) results.

X-Ray Diffraction Analyses

Samples were prepared for XRD analyses by heating under argon at 300 C for two hours to drive off loosely bound and capillary waters. (Thermal analyses had shown little change of other component structure occurs by this "stabilization" treatment.) The samples were mechanically ground and mixed

and either mounted in a Debye-Sherrer camera or in planchet holders and analyzed with CuK_α excitation and a graphite monochrometer to obtain either powder film patterns or strip chart recordings over a 2θ range of 15 to 70 degrees. The resultant powder film patterns were exceedingly complex and difficult to assign d-values and intensities with sufficient accuracies to search X-ray pattern reference files for correct identifications of the component structures present in the samples. The strip chart recordings were somewhat easier to interpret but identifications were hampered by erratic changes attributed to variations in sample orientation, sample thickness and configuration in the beam. To resolve these factors efforts were turned toward the use of a thin sample uniformly dispersed on a silver membrane filter, rotated slowly during the X-ray irradiation. According to Altree-Williams[52] a microsample presented as a thin flat layer has the potential to eliminate or greatly reduce sources of error in quantitative XRD due to variation from calibrating standard to sample in mass absorption, particle size and orientation and degree of crystallinity, all of which can introduce significant systematic errors. The theory developed by Altree-Williams is stated to provide a practical means for compensating for variations in mass absorption. In his work he found that mass absorption coefficients of phases used varied from 35 cm^2/g for α-quartz to 230 cm^3/g for hematite but still the method quantitated these phases in mixtures to ±10 percent accuracy relative to the 1 mg level. He notes that most particulate samples are of small particle size which reduce orientation variations and also notes that the thin layer sample gives very high diffraction intensity relative to its mass, giving detection limits of 20 µg or better depending on the phase considered.

A conventional powder pattern with a planchet holder was compared with one obtained with the sample on a silver membrane filter. The quality of the diffraction patterns appeared equivalent--the planchet technique needed about 200 mg (most of which was recovered) and the silver membrane only 10 mg. A group of Ag filters were run as a check on uniformity based on the peak heights of the Ag lines. These were readily reproducible within ±10 percent as were the Ag line 2θ positions. [Note: The overall technique takes variations among filters into account by running the Ag filters before and after sample loadings.] Next a sample spinner was obtained and aligned in the X-ray beam to ensure good representation of samples loaded into the silver filters. Loading the filters posed a problem. It was impossible to weigh a sample onto the filter and get good uniform distribution due considerably to an electrostatic charge on the filter. However, it was found possible to weigh samples, place them in a small beaker, add Freon TF, ultrasond to obtain a suspension, and then transfer the suspension to an 18-mm I.D. straight sided funnel and, under suction, draw the Freon suspended particulate samples onto the silver filters. This proved successful in giving a uniform thin-layer distribution of 1 to 10 mg quantities of samples on the silver membrane filters.

With the above problems apparently solved, the work turned to selection of reference compounds to further test the procedure. A sea sand was

obtained and, by means of diffractometry, was found to be pure quartz. Similarly, an Fe_2O_3 was run and found to be Fe_2O_3. $PbSO_4$ was prepared from $Pb(NO_3)_2$ and Na_2SO_4 with the precipitate found to be pure $PbSO_4$. A $CaSO_4 \cdot 2H_2O$ was heated for 24 hours at 300 C to $CaSO_4$ anhydrous. These were used to set up reference curves where the weight of a given phase on the filter relates to its diffraction intensity and is independent of the filter loading in the sense that this parameter is determined from silver diffraction line measurements. Quantitation is achieved from measurement of I_{ij} (intensity of diffraction line i of phase j), I_{Ag} (diffraction intensity of the silver line before loading), and I°_{Ag} (diffraction of the silver line after loading).

Continuing this mode of sample preparation analyses and by use of reference components to aid in pattern identification and quantitation, the XRD analyses have proven far more useful in identifying compounds in the oil-fired fly ash samples. An important aspect of the XRD work is the building of a set of XRD reference patterns of known compounds and compound mixes. In this regard it has been found important to check each reference substance to ensure that it is in the proper crystalline and hydration state. Many pure compounds, at least structurally are not as indicated on the bottle label.

Lesser efforts have been expended thus far on the coal fly ash samples. Microscopically these appear to be largely glassy, noncrystalline particles and this is pretty well confirmed by their XRD pattern structures as compared to synthetic standards. The synthetic standards were made from Pyrex glass as a diluent or amorphous phase and quartz, mullite, magnetite, hematite, calcite, orthoclose (feldspar), and gypsum as crystalline phases. The minerals were made up at 5, 10, and 25 percent concentrations in the diluent. The results were far from satisfactory due primarily to the impurity of the minerals used to make the synthetic standards. The experiment was repeated in part using an assayed Alabama sea sand for quartz and chemical pure Fe_2O_3. Patterns derived from these were more typical of those which appeared in the coal fly ash sample pattern structures. Overall the XRD experimental work confirmed that the crystalline components in the coal-fired fly ashes are low in concentrations. Subsequent work is being continued to quantify these ashes by using chemically pure metal oxides and sulfates as reference standards. The crystalline phases definitely identified so far are α-quartz Fe_2O_3, $CaSO_4$, and MgO plus large patterns indicating the presence of large amorphous structures.

Infrared Spectroscopy

The frequency accuracy of Fourier Transform Infrared (FT-IR) and the capability of the FT-IR computer to subtract spectra combined with the use of known reference compounds provide good possibilities of identification of specific inorganic compounds in the fly ash samples. Most efforts have been on the sulfate components of oil-fired fly ash samples. The procedure utilizes the storage capacity of the FTS-14 unit which can handle ~20 low resolution files. This storage capacity is not adequate for the

many compound possibilities encompassed in the fly ash samples but is sufficiently good to develop the methodology. The acquisition of a new FTS-10 has been made and this new unit with its greater resolution, unlimited storage capability, and capacity to work in the far IR region will make it possible to catalog a large library of reference spectra in various hydration states.

Spectra were obtained on several of the reference sulfates potentially present in the samples and these were compared with spectra obtained on the oil fly ash samples. For example, it appeared possible that $MgSO_4$ would be present in oil fly ash No. 1 (per Table 19, $MgSO_4 \cdot H_2O$, ~26.8 percent), so the spectra of No. 1 and $MgSO_4$ were subtracted. This provided added evidence that $MgSO_4$ was present in No. 1 because $MgSO_4$ could be subtracted out without seeing many negative absortpion bands. (Negative absorption bands would appear if the sample did not have bands of the same shape and frequency as the $MgSO_4$ reference spectrum.) The subtraction simplified the remaining sample spectrum permitting the determination that $CaSO_4$ also was present (see Table 19, $CaSO_4$ ~2%). Subtraction of $CaSO_4$ showed that other sulfates were also present.

One problem immediately recognized was the the hydration state of the sample and the reference compound need to be the same in order to successfully identify specific inorganic compounds. As a check on this, several reference compounds were heated nearly to their decomposition states, stored in a vacuum desiccator, and then were run with as little exposure to air as possible. Spectra from these were compared with spectra obtained after allowing the dried references compound stand in air for a short period. In every case splitting seen in the "dry" samples were not observed in the "wet" (atmosphere-exposed) samples. For instance, the 1150 cm^{-1} band in $NiSO_4 \cdot 6H_2O$ was lost after 30 minutes exposure in air which shows that the hydration state can be critically important in identification of specific compounds. Since broad bands (little splitting) are observed in the spectra of the fly ash samples, it is highly useful that they be dried. Attempts were made to recrystallize reference compound in an endeavor to ensure that the entire compound was in a single hydration state. However, the results from this (recrystallization from H_2O) were similar to the effect from samples exposed to moisture--i.e., splitting of the IR bands were lost.

Unfractionated Sample Examinations--

Initially four oil-fired fly ash samples and a synthetic fly ash (containing a number of mixed sulfates with various hydration states) were examined. With the capacity of the FT-IR computer to subtract spectra and with reference compounds and the synthetic ash, listed in Table 21, several sulfates were identified. These were:

TABLE 21. REFERENCE COMPOUND AND MIXTURE USED FOR FTIR ANALYSES

Reference Material	Percent of Total Synthetic Ash	Reference Material	Percent of Total Synthetic Ash
$MgSO_4 \cdot 7H_2O$	20	$CaSO_4 \cdot 2H_2O$	1
MgO	10	CaO	1
$MgSO_4$	5		
$V^{IV}OSO_4 \cdot 3H_2O$	20	$Al_2(SO_4)_3 \cdot 18H_2O$	2
$V^{V}_2O_5$	10	Al_2O_3	1
$Ni^{III}_2O_3 \cdot 6H_2O$	1	Graphite	26
$NiSO_4 \cdot 6H_2O$	1		
$Fe^{III}SO_4 \cdot 7H_2O$	1	Total Synthetic Mixture	100
$Fe^{III}_2O_3$	1		

Synthetic Mixture - $Fe^{III}SO_4 \cdot 7H_2O$; $CaSO_4 \cdot 2H_2O$; $MgSO_4$; $V^{IV}OSO_4 \cdot 3H_2O$

Fly Ash No. 1 - $Fe^{III}SO_4 \cdot 7H_2O$; $CaSO_4$ $2H_2O$; $MgSO_4$

Fly Ash No. 2 - $Fe^{III}SO_4 \cdot 7H_2O$ possibly; $MgSO_4$ possibly; $VOSO_4 \cdot 3H_2O$ possibly; an unidentified band

Fly Ash No. 4 - $Fe^{III}SO_4 \cdot 7H_2O$ possibly, $CaSO_4 \cdot 2H_2O$; and unidentified band - possibly $V(SO_4)_2$ or $VOSO_4$

Fly Ash No. 5 - $Fe^{III}SO_4 \cdot 7H_2O$ possibly; $MgSO_4$ possibly; $VOSO_4 \cdot 3H_2O$ possibly; a large unidentified band.

As listed above there is an unknown sulfate present in the Nos. 2, 4, and 5 samples which has (among others) absorption bands near 990 and 1050 cm^{-1}. The unknown closely resembles the reference spectrum of the $VOSO_4 \cdot 3H_2O$ except for the 990 and 1050 cm^{-1} bands. The intensities of the unknown roughly follows the known vanadium concentrations in Samples 2, 4, and 5 and was not seen in the No.1 sample in which the vanadium concentration is low. The spectra of the unknown and the spectrum of the $VOSO_4 \cdot 3H_2O$ are the only sulfates showing a band at 490 cm^{-1}.

A sample of vanadium sulfate (ICN Pharmaceuticals) was obtained and its spectrum run and stored in the computer memory. This spectrum shows bands at 990 and 1050 cm^{-1} which were seen in the Nos. 2, 4, and 5 samples. However, its spectrum shows a complex splitting in the 600 to 700 cm^{-1} region and shows an abnormally high ratio of the intensities of the 990 and 1050 cm^{-1} bands to the intensities of the S-O vibrations near 1100 cm^{-1}. This may be due to a mixture of hydrated forms. This complex splitting and the intensity ratio change is not seen in the fly ash samples and makes computer subtraction difficult.

Computer subtractions were made of the synthetic mixture (see Table 21. Infrared bands were seen which indicated the presence of $MgSO_4$ (or hydrates). A spectrum of $MgSO_4$ was subtracted from the spectrum of the synthetic mixture. This simplified the resultant spectrum in the 1100 cm^{-1} region so that $Fe_2(SO_4)_3$ was detected. Succeedingly by subtraction, $CaSO_4$ and $VOSO_4$ also were detected and subtracted from the spectrum of the mixture and at this point the resultant spectrum was nearly a straight line. The $Al_2SO_4 \cdot 18H_2O$ and $NiSO_4 \cdot 6H_2O$, possibly present in the mixture in low concentractions, were not detected. This work on the synthetic mixture showed that computer subtractions could successfully identify inorganic sulfate when appropriate reference compounds are available.

Because of the problems in obtaining the appropriate vanadium sulfate or oxysulfate reference compound, computer subtractions of the fly ash samples Nos. 2, 4, and 5 have not worked well. As discussed above for fly ash No.1 (which contains low vanadium as indicated by the water soluble

determination), $MgSO_4$ was subtracted successfully permitting the identification of $Fe_2(SO_4)_3$ in the resultant spectrum. The presence of $CaSO_4$ is indicated by a band in the 670 cm^{-1} region but after subtracting the spectra of $MgSO_4$ and $Fe_2(SO_4)_3$, the 1100 cm^{-1} causing broadening of the bands. Since the computer subtraction worked well for the synthetic mixture and not as well for the fly ash samples, the problem may be due to the presence of mixed cation sulfates.

Water Soluble Fractions IR Examination--

Spectra were obtained on the water soluble fractions of the oil-fired fly ash samples Nos. 1, 2, 4, and 5 in the hope of gaining increased detection and some simplification of spectra. These fractions were dried and baked under argon at 350 C. In each case the spectrum of the water soluble portion was better defined (more splitting) in the 1100 cm^{-1} region and in the 650 cm^{-1} region. It appeared as if broad underlying absorptions were removed. This better definition was most pronounced for the No. 1 sample.

The spectra obtained on these water soluble extracts, dried, heated under argon and presumably in the same hydration state after mathematical subtraction against stored reference spectra showed:

(a) Oil-fired fly ash No.1 showed a predominance of $MgSO_4$ anhydrous and lesser amounts of $CaSO_4$. Much improved subtraction matches were obtained indicating that the $MgSO_4$ had been in a hydration state other than the stored $MgSO_4 \cdot 7H_2O$ or anhydrous $MgSO_4$. Subtraction of the $MgSO_4$ component left a 670 cm^{-1} and a 1170 cm^{-1} band of $CaSO_4$. Na_2SO_4 and $FeSO_4$ previously seen were not confirmed nor was the positive presence of $VOSO_4$ although there were indications of its presence. ($MgSO_4$, $Fe_2(SO_4)_3$, and $CaSO$ had been detected in the unfractionated samples in previous IR runs.)

(b) Oil-fired fly ash No.2 did not show a predominance of any one component, nor was a good matched obtained to the stored reference spectra which suggest the presence of mixed cation sulfates, discussed later. $VOSO_4$, V_2SO_4, $MgSO_4$, $CaSO_4$, and $NiSO_4$ all are possibly present in this treated water soluble fraction. ($MgSO_4$, $FeSO_4$, $VOSO_4$, and an unidentified sulfate band had been detected in the total sample.)

(c) The treated water soluble fraction of oil-fired fly ash No.4 showed some changes over the untreated sample fraction as evidenced by the loss of a few bands. The major change was a sharpening of the 1200 to 1100 cm^{-1} region into one intense 1160 cm^{-1} band. Subtractions yielded a band at 870 cm^{-1} of moderate intensity and a weak 1400 cm^{-1} both of which are present in the unfractionated No.6 sample but not as yet identified.

Based on chemical analyses similarities, an ammonium sulfate is suggested for the No. 4 and No. 6 samples. The No. 4 treated water soluble fraction has a large amount of $V(SO_4)_2$ plus $MgSO_4$ and $NiSO_4$. The $V(SO_4)_2$ spectra in the treated No. 4 are similar to $VOSO_4$ so it could be present at least in minor quantities.

(d) The treated water soluble No. 5 fraction showed changes from the nonheated fraction notably showing sharper absorption bands and fewer bands indicating the probability of having a greater percentage of the sample in a single hydration state. The sample had a large amount of $VOSO_4$. Subtracting this from the spectrum, although the subtraction was not perfect, it was possible to identify the presence of $MgSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$. (Prior work on the unfractionated sample had shown the presence of $VOSO_4 \cdot 3H_2O$, $Fe_2(SO_4)_3 \cdot 7H_2O$, $MgSO_4$, and an unidentified sulfate band.)

Total Sample IR Examination of No. 6 Oil Fly Ash--

Oil fly ash No. 6 was examined by IR. From comparison with reference spectra and literature spectra, it was possible to identify:

- A predominant component indicated by a very sharp band at 1400 cm^{-1} of NH_4HSO_2--this is in agreement with analyzed chemical data, although the possibility of $(NH_4)_2SO_4$ or a mixture of the two salts exists. Minor components of $MgSO_4$, $NiSO_4$, and $CaSO_4$ were identified.

No work has been done on the water soluble fraction of No. 6.

Mixed Sulfates IR Experiments--

The soluble fraction of sample No. 2 did not show a predominance of any one component suggesting a possibility that mixed sulfates may form when several sulfates are dissolved together, taken to dryness and baked. This was noticeable in the No. 2 sample spectrum where there seem to be some sort of interaction occurring among the various components making it difficult to sort out and assign absorption bands. It is thought that a mixed sulfate could form if for example a magnesium cation were to displace a vanadium cation in the vanadium salt lattice on dissolution, evaporation to dryness and heating. Such a mixed sulfate, if formed, would be expected to display a spectrum different from either of the parent sulfates due to lattice changes. To investigate this a mixture of 46 percent $VOSO_4 \cdot 5H_2O$, 41 percent $MgSO_4 \cdot 7H_2O$, and 13 percent $NiSO_4 \cdot 6H_2O$ was prepared and divided into five portions.

Four of the portions were taken up in solution after which they were recovered simply by evaporating the water off. The fifth portion was

examined spectroscopically as just the physical mix of the sulfates to serve as a comparison with the dissolved samples. The four recovered samples were treated as follows:

- The first was simply air dried
- The second was baked overnight at 80 C in air
- The third was baked overnight at 120 C under argon
- The fourth was baked overnight at 350 C under argon.

The samples were then run in the usual KBr pellet fashion, and then all five were compared to each other and to a computer generated synthetic spectra derived from previously stored reference spectra.

Figures 2 and 3 show the spectra of the five fractions and also the computer generated spectrum. Figure 4 illustrates the stored reference spectrum of $NiSO_4 \cdot 6H_2O$, $VOSO_4 \cdot 5H_2O$, and $MgSO_4 \cdot 7H_2O$. From these spectra, the following may be deduced:

(1) Allowing for the fact that the stored reference spectra of $MgSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, and $VOSO_4$ do not exactly match the actual $MgSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, and $VOSO_4 \cdot 5H_2O$ used in this study, it seems that the physical mixture of the sulfates, before they were dissolved, matches fairly well with the computer generated spectra. This is of course not at all surprising.

(2) In Figure 2, the spectra of the mixture of sulfates recovered from solution is quite different from that of the sulfates before they were dissolved.

(3) There are some minor differences in band intensity between the unbaked sample and that baked at 80 C overnight, but there is virtually no difference at all between the samples baked at 80, 120, and 350 C. (The difference in ratio of the 1100 to 1200 cm^{-1} band in the 120 C sample spectra is a computer artifact.

(4) The difference between the baked and unbaked samples seems to be primarily a sharpening of the bands in the baked samples. Thus, it is useful to bake the samples to sharpen the bands and also to help achieve a reproducible hydration state.

(5) The amazing similarity between the three baked spectra illustrates two important points:

    (a) Once the water has been driven off, no further changes occur in the sulfate lattice

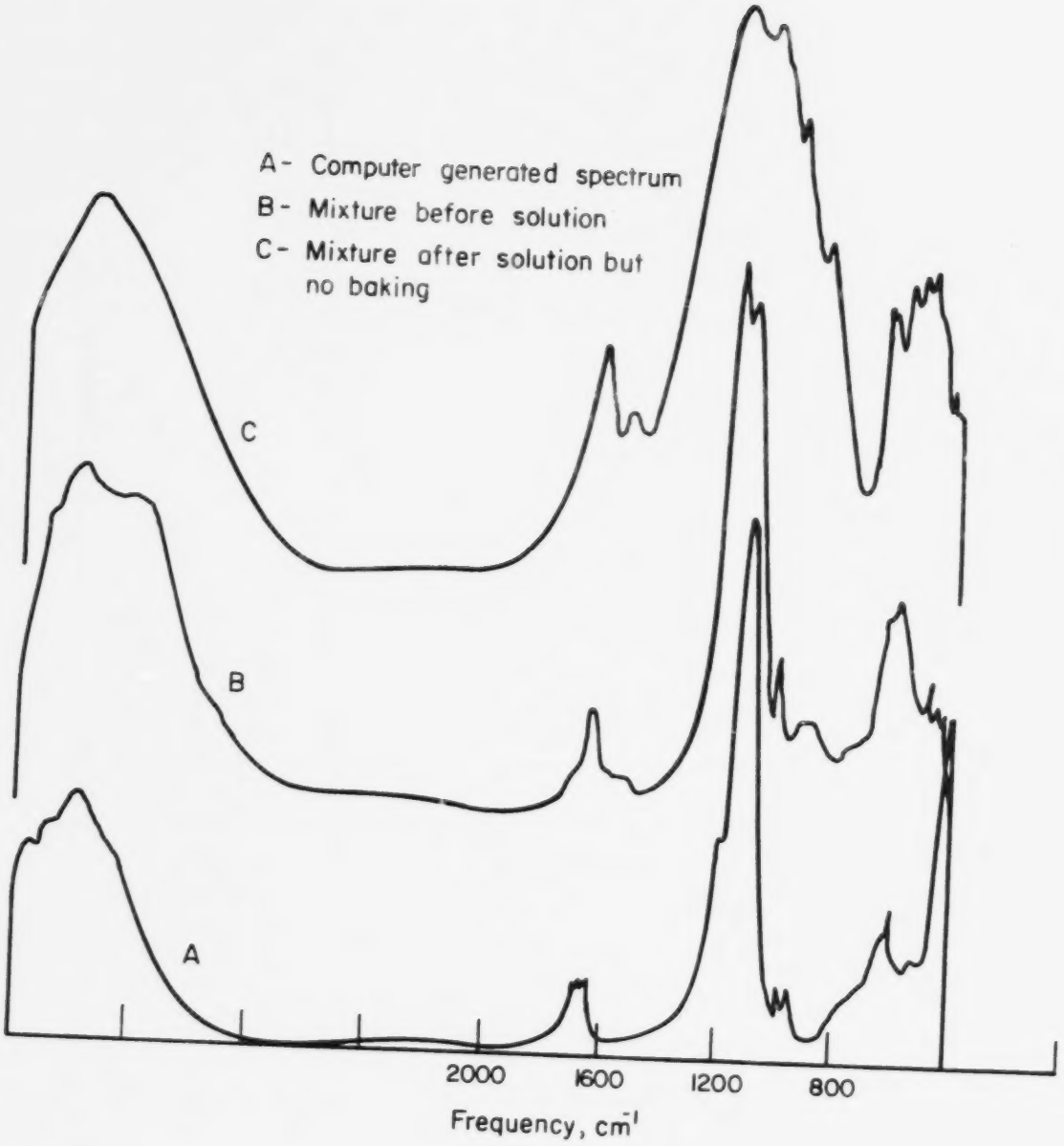

FIGURE 2. SPECTRA OF COMPUTER GENERATED SPECTRUM (A), MIXTURE BEFORE SOLUTION (B), AND MIXTURE AFTER SOLUTION AND AIR DRIED (C).

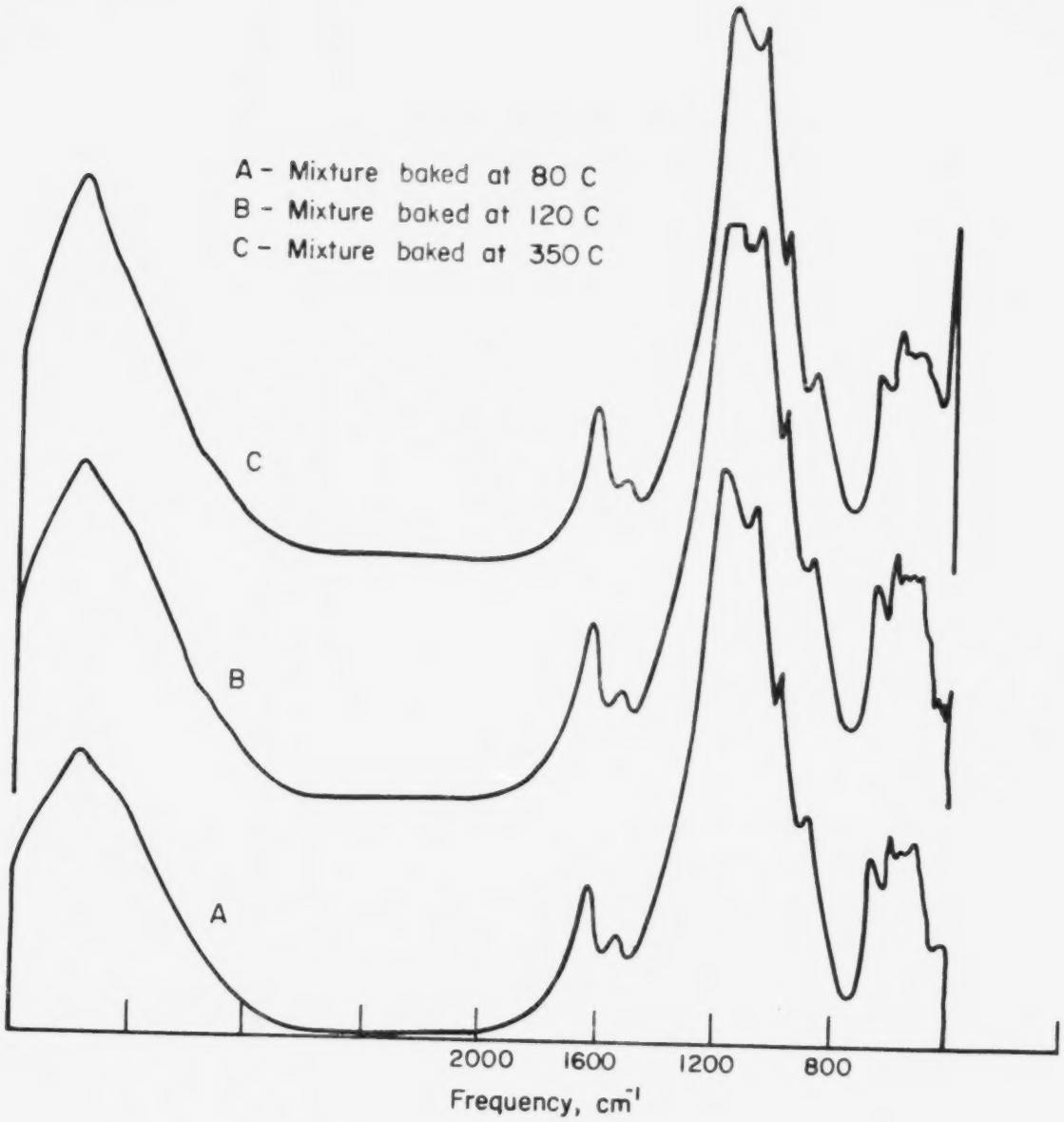

FIGURE 3. SPECTRA OF MIXTURES DISSOLVED, DRIED AND BAKED AT 80 C (A), AT 120 C (B), AND 350 C (C)

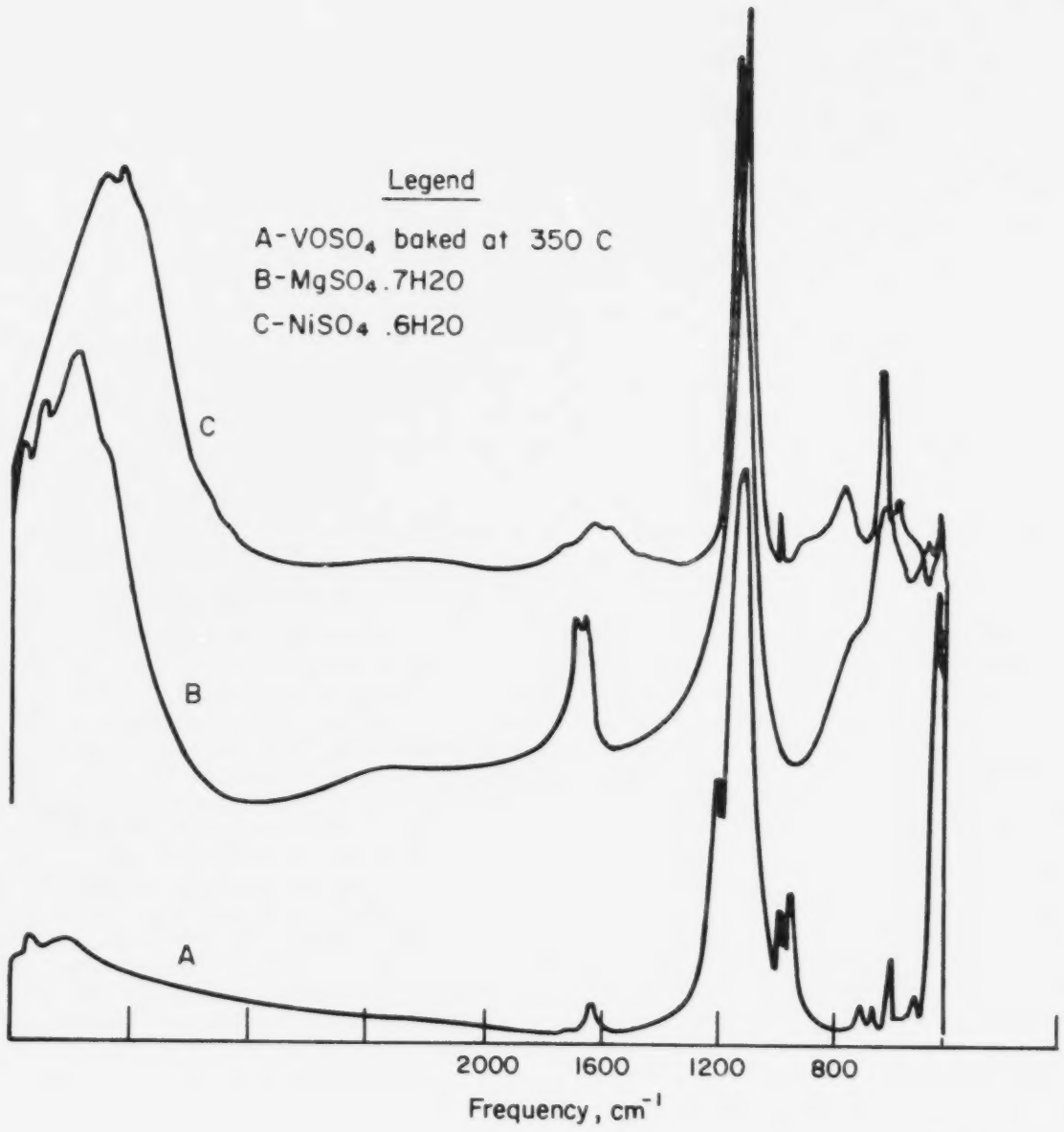

FIGURE 4. STORED REFERENCE SPECTRA

(b) The sample handling technique, including the manufacture of our KBr pellets, seems to be quite reproducible.

In spite of the major changes which occur upon dissolution of a mixture of sulfates, it is still felt that the major components can be accurately identified assuming the appropriate precautions are taken. One factor which helps identification of components is that, while the sulfate bands in the spectra of a dissolved mixture of sulfates broaden, they do not completely disappear, nor do new bands appear. This factor, coupled with having the proper reference spectra in the proper hydration state on file, should allow, through spectra subtraction, the identification of the unknown sulfate(s). Also running the ash sample before the soluble fraction is extracted (as was done on oil ash No. 6) gives a before and after solution spectra for comparison purposes. Computer generated spectra are still of great value in spectral matching; however, it will probably be advisable to start running synthetic mixtures in the future for those samples demonstrating more than one sulfate in major proportions. Running synthetic mxitures which had been dissolved would be advisable for the following reason: Even if reference spectra are available before and after solution and baking, it is not expected that the large degree of broadening of the sulfate band between 1000 and 1200 cm^{-1} in these reference spectra will be seen. It is believed that the sulfate broadening is due to the mixed sulfates discussed previously.

The effect of having various cations in the sulfate's lattice is to "smear" energy levels and thus broaden existing bands. The only way to accurately duplicate the spectrum of a mixed sulfate is to prepare a synthetic mixture and dissolve it so that smearing of the sulfate bands occurs Preparation of these synthetic mixed sulfates should not be required for the identification of the two or perhaps three major components in an unknown, but the detection of minor components will only be possible if reference spectra of this nature are available to perform subtractions with. It is appropriate to emphasize at this point that this mixed sulfate phenomena will only be a problem when more than one sulfate is present in large amounts in the unknown sample. To date only fly ash No. 2 has presented this difficulty. To summarize, one needs to be aware that spectral changes of fair magnitude do occur upon the dissolution of a mix of sulfates containing more than one predominant component, presumably due to band broadening caused by the formation of a mixed sulfate. Baking the recovered sample is advisable, and the identification of minor components by FT-IR will require the actual preparation of synthetic mixed sulfates which could then be mathematically manipulated by the computer. In general, the FT-IR has indicated that examination of a fly ash should include a spectrum before water extraction, after water extraction, and after water extraction and baking under argon at 350 C.

Preliminary Evaluation of Calculated Equilibrium Fly Ash Compositions

A preliminary evaluation was made of the usefulness of equilibrium thermodynamic calculations for predicting the composition of fly ash from a particular fuel. For this evaluation a comparison was made of previous calculations for a "typical" No. 6 fuel oil (Kircher, et al., EPA-600/7-77-041) with analyses of oil-fired fly ashes Nos. 1, 2, and 4 (Table 19).

To make the desired comparisons, some assumptions were required. Since the thermodynamic calculations were based on equilibrium, there would be no unburned carbon in the presence of excess air or oxygen. However, in real fly ash there is always carbon present and it can be large fraction of the fly ash. Since the carbon is essentially inert, it was subtracted from the fly ash analysis and the distribution of metal oxides and sulfates recalculated on a mole percent basis.

The analyzed fly ashes have large amounts of MgO and $MgSO_4$ because additives were used for corrosion control in the combustion systems from which samples were obtained. The calculated fly ash compositions did not assume any additive. In order to compare the calculated and measured values it was assumed that 95 percent of the Mg in the actual fly ash samples resulted from the additive and this was subtracted from the sample analyses so they could be compared more directly with the thermodynamic calculations.

The measured data for No. 6 fuel oil fired fly ash are based on oil fired fly ash samples Nos. 1, 2, and 4 (Table 19). A range is indicated in the accompanying Table 22 for the minimum and maximum reported concentration for the three samples. The reported values for V_2O_5 and $VOSO_4$ have been summed since $VOSO_4$ was not included in the thermodynamic calculations so results can only be compared on the basis of total vanadium. Also, several oxides, e.g., NiO, were calculated to be below analytical detection limits but in fact were observed. Such differences are to be expected, however, since the actual fuel ash compositions are not well known and are undoubtedly different from the composition assumed in the calculations.

Recognizing the fuel compositions are different, the agreement between calculated and measured values is about as good as one could expect. The larger relative amounts of iron and silicon in the calculated fly ash, for instance, could simply reflect the difference between assumed "typical" fuel and that actually used in the tests. It must also be remembered that the amount of Mg additive assumed and corrected for was completely arbitrary. If the calculations had been based on the actual fuel composition, the results would very likely have shown much better agreement.

Further comparisons of this type are not warranted at this time because of the differences in fuel compositions. However, since the preliminary results are promising, the calculations should be redone using known fuel compositions Nos. 2, 4, 5, and 6. The predicted calculations using the known fuel compositions could aid the analytical efforts by

identifying low concentration species which could be observed and also by confirming the possible existence of unexpected but observed species. (Note: It is anticipated that the high concentration components can be obtained directly using the developed methodologies.) An end result might be predictions of trace metal compositions from the fuel compositions.

TABLE 22. COMPARISON OF CALCULATED AND MEASURED FLY ASH COMPOSITIONS

Calculated		Measured
SiO_2	31.8	1.2 - 1.9
Al_2O_3	12.8	0.8 - 4.5
$Al_2(SO_4)_3$	11.2	0.7 - 10.4
Fe_2O_3	6.4	0.8 - 1.5
$FeSO_4$	11.2	1.3 - 3.3
V_2O_5	11.4	15 - 73
$VOSO_4$	--	
MgO	0*	0.2 - 3.7
$MgSO_4$	4.2	1.4 - 3.8
NiO	0*	0.8 - 2.8
$NiSO_4$	3.4	7.3 - 8.6
Na_2SO_4	2.7	4.1 - 39.3
CaO	0*	0.1 - 1.8
$CaSO_4$	1.5	0.7 - 6.5
$CoSO_4$	0.8	1.6 - 4.2**
Cr_2O_4	0.5	
TiO_2	0.5	

* Less than 0.03

** Other sulfates and oxides

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APPENDIX A

COMPOSITIONS OF CRUDES FROM VARIOUS ORIGINS

Tables A-1 through A-5 are taken from Tables 13, 14, 17, 18, and 19, respectively, of Report PB-225-039 prepared by Magee, Hall, and Varga of Esso Research and Engineering Company for the U.S. Environmental Protection Agency.

TABLE A-1

SULFUR AND NITROGEN CONTENT
OF THE GIANT U.S. OIL FIELDS

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
ALABAMA			
Citronelle	0.38	0.02	6,390
ALASKA			
Granite Point	0.02	0.039	5,552
McArthur River	0.16	0.160	40,683
Middle Ground Shoal	0.05	0.119	11,277
Prudhoe Bay (North Slope)	1.07	0.23	1,076
Swanson River	0.16	0.203	11,709
APPALACHIAN			
Allegany	0.12	0.028	388
Bradford	0.11	0.010	2,470
ARKANSAS			
Magnolia	0.90	0.02	850
Schuler and East	1.55	0.112	800
Smackover	2.10	0.08	2,800
CALIFORNIA			
SAN JOAQUIN VALLEY			
Belridge South	0.23	0.773	9,211
Buena Vista	0.59	--	5,429
Coalinga	0.43	0.303	7,866
Coalinga Nose	0.25	0.194	4,752
Coles Levee North	0.39	0.309	1,006
Cuyama South	0.42	0.337	2,034
Cymric	1.16	0.63	3,345
Edison	0.20	0.446	1,417
Elk Hills	0.68	0.472	951
Fruitvale	0.93	0.527	1,109
Greeley	0.31	0.266	761
Kern Front	0.85	0.676	3,440
Kern River	1.19	0.604	25,542
Kettleman North Dome	0.40	0.212	840
Lost Hills	0.33	0.094	2,328
McKittrick - Main Area	0.96	0.67	5,348
Midway Sunset	0.94	0.42	33,583
Mount Poso	0.68	0.475	1,378
Rio Bravo	0.35	0.158	425
COASTAL AREA			
Carpenteria Offshore	--	--	5,295
Cat Canyon West	5.07	0.54	2,705
Dos Cuadras	--	--	27,739
Elwood	--	--	108

* Oil and Gas Journal, January 31, 1972 pp. 95-100.

TABLE A-1 (Cont'd)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
Orcutt	2.48	0.525	2,173
Rincon	0.40	0.48	4,580
San Ardo	2.25	0.913	9,939
Santa Ynez**	--	--	--
Santa Maria Valley	4.99	0.56	1,966
South Mountain	2.79	--	1,962
Ventura	0.94	0.413	10,188
LOS ANGELES BASIN			
Beverly Hills	2.45	0.612	8,400
Brea Olinda	0.75	0.525	4,228
Coyote East	0.95	0.336	864
Coyote West	0.82	0.347	2,436
Dominguez	0.40	0.360	1,717
Huntington Beach	1.57	0.648	16,249
Inglewood	2.50	0.640	3,992
Long Beach	1.29	0.55	3,183
Montebello	0.68	0.316	740
Richfield	1.86	0.575	1,910
Santa Fe Springs	0.33	0.271	953
Seal Beach	0.55	0.394	1,468
Torrance	1.84	0.555	1,338
Wilmington	1.44	0.65	72,859
COLORADO			
Rangely	0.56	0.073	10,040
FLORIDA			
Jay	0.32	0.002	.370
ILLINOIS			
Clay City	0.19	0.082	4,650
Dale	0.15	0.080	690
Loudon	0.27	0.097	4,420
New Harmony	0.23	0.158	2,740
Salem	0.17	0.102	3,360
KANSAS			
Bemis-Shutts	0.57	0.162	2,590
Chase-Silica	0.44	0.13	1,600
Eldorado	0.18	0.085	1,500
Hall-Gurney	0.34	0.108	2,480
Kraft-Prusa	0.27	0.171	3,200
Trapp	0.41	0.076	1,930
LOUISIANA			
NORTH			
Black Lake	--	--	--
Caddo-Pine Island	0.37	0.026	3,500
Delhi	0.82	0.053	5,870
Haynesville (Ark.-La.)	0.66	0.022	2,730
Homer	0.83	0.081	330
Lake St. John	0.17	--	1,170
Rodessa (La.-Tex.)	0.46	0.032	900

* Oil and Gas Journal, January 31, 1972, pp. 95-100.

** Undeveloped field, Santa Barbara Channel. Uncorroborated estimate of reserves of 1 to 3 billion bbl.

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TABLE A-1 (Cont'd.)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
OFFSHORE			
Bay Marchand Block 2 (Incl. onshore)	0.46	0.11	30,806
Eugene Island Block 126	0.15	0.030	5,621
Grand Isle Block 16	0.18	0.04	21,681
Grand Isle Block 43	--	--	22,776
Grand Isle Block 47	0.23	0.04	4,271
Main Pass Block 35	0.19	0.071	3,504
Main Pass Block 41	0.16	0.025	18,469
Main Pass Block 69	0.25	0.098	12,775
Ship Shoal Block 208	0.38	0.02	10,038
South Pass Block 24 (Incl. onshore)	0.26	0.068	20,330
South Pass Block 27	0.18	0.049	21,425
Timbalier S. Block 135	0.66	0.088	13,578
Timbalier Bay (Incl. onshore)	--	--	
West Delta Block 30	0.33	0.081	30,988
West Delta Block 73	0.33	0.09	26,390
SOUTH, ONSHORE	--	--	15,987
Avery Island	0.12	--	3,400
Bay De Chene	0.27	0.060	6,643
Bay St. Elaine	0.39	0.04	7,775
Bayou Sale	0.16	--	5,293
Black Bay West	0.19	0.04	9,892
Caillou Island (Incl. offshore)	0.23	0.04	31,828
Cote Blanche Bay West	0.16	0.033	15,658
Cote Blanche Island	0.10	0.01	8,797
Delta Farms	0.26	0.055	1,278
Garden Island Bay	0.22	0.06	16,096
Golden Meadow	0.18	--	2,738
Grand Bay	0.31	--	6,680
Hackberry East	0.30	0.054	2,226
Hackberry West	0.29	--	3,760
Iowa	0.20	0.039	876
Jennings	0.26	--	292
Lafitte	0.30	--	10,877
Lake Barre	0.14	0.02	7,592
Lake Pelto	0.21	0.035	4,891
Lake Salvador	0.14	0.02	4,380
Lake Washington (Incl. offshore)	0.37	0.146	10,913
Leeville	0.20	0.019	4,343
Paradis	0.23	--	1,898
Quarantine Bay	0.27	0.061	7,117
Romere Pass	0.30	--	3,759
Venice	0.24	--	5,475
Vinton	0.34	0.044	2,299
Weeks Island	0.19	--	10,183
West Bay	0.27	0.071	9,563

* Oil and Gas Journal, January 31, 1972, pp. 95-100.

TABLE A-1 (Cont'd.)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Product (Thousands of Barrels)*
MISSISSIPPI			
Baxterville	2.71	0.111	9,300
Heidelberg	3.75	0.112	3,450
Tinsley	1.02	0.08	2,450
MONTANA			
Bell Creek	0.24	0.13	5,950
Cut Bank	0.80	0.055	5,180
NEW MEXICO			
Caprock and East	0.17	0.034	905
Denton	0.17	0.014	2,350
Empire Abo	0.27	0.014	9,520
Eunice	1.14	0.071	1,330
Hobbs	1.41	0.08	5,700
Maljamar	0.55	0.062	6,040
Monument	1.14	0.071	3,720
Vacuum	0.95	0.075	17,030
NORTH DAKOTA			
Beaver Lodge	0.24	0.019	3,140
Tioga	0.31	0.016	1,790
OKLAHOMA			
Allen	0.70	0.21	2,920
Avant	0.18	--	365
Bowlegs	0.24	0.140	2,260
Burbank	0.24	0.051	5,240
Cement	0.47	0.152	2,370
Cushing	0.22	0.08	4,300
Earlsboro	0.47	--	765
Edmond West	0.21	0.045	730
Eola-Robberson	0.35	0.115	4,850
Fitts	0.27	--	1,420
Glenn Pool	0.31	0.096	2,480
Golden Trend	0.15	0.15	12,330
Healdton	0.92	0.15	4,600
Hewitt	0.65	0.148	5,660
Little River	0.28	0.065	440
Oklahoma City	0.16	0.079	1,750
Seminole, Greater	0.30	0.016	1,640
Sho-Vel-Tum	1.18	0.27	36,500
Sooner Trend	--	--	15,240
St. Louis	0.11	0.04	1,350
Tonkawa	0.16	0.033	290

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

TABLE A-1 (Cont'd.)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
TEXAS			
DISTRICT 1			
Big Wells	--	--	5,840
Darst Creek	0.78	0.075	1,971
Luling-Branyon	0.86	0.110	1,679
DISTRICT 2			
Greta	0.17	0.038	3,577
Refugio	0.11	0.027	657
Tom O'Connor	0.17	0.038	23,360
West Ranch	0.14	0.029	17,009
DISTRICT 3			
Anahuac	0.23	0.041	9,052
Barbers Hill	0.27	0.06	766
Conroe	0.15	0.022	12,994
Dickison-Gillock	0.82	0.014	2,920
Goose Creek and East	0.13	0.028	1,095
Hastings E&W	0.20	0.03	17,191
High Island	0.26	0.048	2,081
Hull-Merchant	0.35	0.081	1,643
Humble	0.46	0.097	1,241
Liberty South	0.14	0.044	949
Magnet Withers	0.19	0.033	3,869
Old Ocean	0.14	0.029	1,132
Raccoon Bend	0.19	0.048	2,409
Sour Lake	0.14	0.016	1,058
Spindletop	0.15	0.03	328
Thompson	0.25	0.029	12,885
Webster	0.21	0.046	16,206
West Columbia	0.21	0.055	1,351
DISTRICT 4			
Agua Duke-Stratton	<.1	0.015	2,518
Alazan North	0.04	0.014	3,723
Borregas	<.1	0.029	4,818
Government Wells N.	0.22	0.043	511
Kelsey	0.13	0.008	6,059
La Gloria and South	<.1	0.008	936
Plymouth	0.15	0.049	986
Seeligson	<.1	0.015	6,424
Tijerina-Canales-Blucher	<.1	0.010	5,986
White Point East	0.13	0.02	1,606
DISTRICT 5			
Mexia	0.20	0.048	109
Powell	0.31	0.054	109
Van and Van Shallow	0.8	0.039	12,337

* Oil and Gas Journal, January 31, 1972, pp. 95-100.

TABLE A-1 (Cont'd.)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
DISTRICT 6			
East Texas	0.32	0.066	71,139
Fairway	0.24	--	14,271
Hawkins	2.19	0.076	29,054
Neches	0.13	0.083	3,942
New Hope	0.46	0.007	292
Quitman	0.92	0.036	3,103
Talco	2.98	--	4,380
DISTRICT 7-C			
Big Lake	0.26	0.071	474
Jameson	<.1	0.034	1,387
McCamey	2.26	0.139	985
Pegasus	0.73	0.200	4,052
DISTRICT 8			
Andector	0.22	0.033	5,694
Block 31	0.11	0.032	6,242
Cowden North	1.89	0.095	9,782
Cowden South, Foster, Johnson	1.77	0.127	14,198
Dollarhide	0.39	0.074	7,592
Dora Roberts	<.1	0.023	3,066
Dune	3.11	0.111	11,425
Emma and Triple N	<.1	0.025	3,030
Fuhrman-Mascho	2.06	0.085	1,935
Fullerton	0.37	0.041	6,607
Goldsmith	1.12	0.079	20,951
Headlee and North	<.1	0.083	1,460
Hendrick	1.73	0.094	766
Howard Glasscock	1.92	0.096	6,606
Iatan East	1.47	0.120	3,687
Jordan	1.48	0.10	3,212
Kermit	0.94	0.092	2,007
Keystone	0.57	0.042	8,322
McElroy	2.37	0.080	9,015
Means	1.75	0.205	7,921
Midland Farms	0.13	0.080	6,059
Penwell	1.75	0.205	2,044
Sand Hills	2.06	0.085	6,606
Shafter Lake	0.25	0.041	2,956
TXL	0.36	0.067	4,854
Waddell	1.69	0.098	4,453
Ward South	1.12	0.08	803
Ward Estes North	1.17	0.107	10,184
Yates	1.54	0.150	13,359

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

TABLE A-1 (Cont'd.)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
DISTRICT 8-A			
Cogdell Area	0.38	0.063	14,235
Diamond M	0.20	0.131	7,373
Kelly-Snyder	0.29	0.066	52,487
Levelland	2.12	0.136	9,746
Prentice	2.64	0.117	5,913
Robertson	1.37	0.100	2,774
Russell	0.77	0.078	4,234
Salt Creek	0.57	0.094	9,271
Seminole	1.98	0.106	9,125
Slaughter	2.09	--	35,515
Spraberry Trend	0.18	0.173	18,688
Wasson	1.14	0.065	51,210
DISTRICT 9			
KMA	0.31	0.068	2,920
Walnut Bend	0.17	0.05	3,942
DISTRICT 10			
Panhandle	0.55	0.067	14,235
UTAH			
Greater Aneth	0.20	0.059	7,660
Greater Redwash	0.11	0.255	5,800
WYOMING			
Elk Basin (Mont.-Wyo.)	1.78	0.185	14,380
Garland	2.99	0.290	3,500
Grass Creek	2.63	0.311	3,760
Hamilton Dome	3.04	0.343	4,500
Hilight	--	--	11,300
Lance Creek	0.10	0.055	325
Lost Soldier	1.21	0.076	4,820
Oregon Basin	3.44	0.356	12,260
Salt Creek	0.23	0.109	11,750

* Oil and Gas Journal, January 31, 1972, pp. 95-100.

TABLE A-2

TRACE ELEMENT CONTENT OF U.S. CRUDE OILS

State and Field	Trace Element, ppm V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	Ag	Analytical Method
ALABAMA										Emission spectroscopy
Toxey	9	14								Emission spectroscopy
Toxey	10	16								
ALASKA										Emission spectroscopy
Kuparuk, Prudhoe Bay	32	13								Emission spectroscopy
Kuparuk, Prudhoe Bay	28	12								Emission spectroscopy
McArthur River, Cook Inlet	nd	nd								Emission spectroscopy
Prudhoe Bay	31	11								Emission spectroscopy
Put River, Prudhoe Bay	16	6								Emission spectroscopy
Redoubt Shoal, Cook Inlet	nd	4								
Trading Bay, Cook Inlet	nd	nd								
ARKANSAS										Emission spectroscopy
Brister, Columbia	nd	nd								Emission spectroscopy
El Dorado, East	12	11								Emission spectroscopy
Schuler	15.2	10.3	1.2	<1	<1	<1	nd	nd		Emission spectroscopy
Smackover	nd	4								Emission spectroscopy
Stephens-Smart	18.5	22.7	6.3	<1	<1	<1	nd	<1		Emission spectroscopy
Tubal, Union	nd	nd								Emission spectroscopy
West Atlanta	<1	<1	<1	<1	<1	<1	nd	nd		
CALIFORNIA										Emission spectroscopy
Ant Hill	14.3	66.5	28.5	<1	<1	nd	nd	nd		Emission spectroscopy
Arwin	9.0	28.0								(1)
Bradley Sands	134.5	--								Emission spectroscopy
Cat Canyon	128	75								Emission spectroscopy
Cat Canyon	209	102								Emission spectroscopy
Coalinger	5.1	21.9	5.1	<1	<1	<1	<1	nd		Emission spectroscopy
Coal Oil Canyon	6.0	20.0								Emission spectroscopy
Coles Levee	11.0	31.0								Emission spectroscopy
Coles Levee	2.2	21.6	2.2	<1	<1	nd	<1	nd		Emission spectroscopy
Cuyama	10.0	32.0								Emission spectroscopy
Cymric	30.0	43.0								Emission spectroscopy
Cymric	0.8	2.3	2.0							2.6, 2.4, 1.9 Emission spectroscopy
Cymric										Emission spectroscopy
Cymric	0.6	1.1	2.0							21.0, 14.0, 2.9 Emission spectroscopy
Cymric										Emission spectroscopy
Cymric	1.0	2.0	2.0							Emission spectroscopy
Edison	6.0	11.0								Emission spectroscopy
Elk Hills	8.3	38.5	38.5	<1	<1	<1	<1	nd		Emission spectroscopy
Elwood South	nd	11								X-ray fluorescence
Gibson	37	125								Emission spectroscopy
Gots Ridge	188	80								Emission spectroscopy
Helm	14.0	27.0								Emission spectroscopy
Helm	2.5	10.5	2.5	<1	<1	nd	nd	<1		Emission spectroscopy
Huntington Beach	29	104								Emission spectroscopy
Inglewood	125.7	125.7	125.7	<1	1.3	nd	<1	nd		Colorimetric
Kettleman	34.0	35.0	24.0							(1)
Kettleman Hills	11.0	24.0								(1)
Las Flores	106.5	--								(1)
Lompoc	37.6	--								Emission spectroscopy
Lompoc	199	90								Emission spectroscopy
Lost Hills	39.0	8.0								Emission spectroscopy
Midway	82.6	82.6	82.6	1.8	1.8	<1	<1	nd		(1)
Nicolai	246.5	--								X-ray fluorescence (inter. std)
North Belridge	--	107								Colorimetric
North Belridge	--	80								Emission spectroscopy
North Belridge	--	83								X-ray fluoresc. (ext. std.)
North Belridge	23	83								(1)
Orcutt	162.5	--								(1)
Oxnard	40?.5	--								(1)
Purisma	218.5	--								Emission spectroscopy
Raisin City	8.0	21.0								

(1) Not specified.

nd Sought but not detected.

TABLE A-2 (Cont'd)

State and Field	Trace Element, ppm V	Ni	Fe	Ba	Cr	Mo	Mo	Sn	As	Analytical Method
Rio Bravo	--	2.2								X-ray fluorescence (int. std.)
Rio Bravo	--	--	2.6							X-ray fluorescence (int. std.)
Rio Bravo	--	--	2.5							Emission spectroscopy
Russell Ranch	12.0	26.0								Emission spectroscopy
San Joaquin	44.8	--								(1)
Santa Maria	223	97	17							Colorimetric
Santa Maria	202	--								(1)
Santa Maria	180	106								Emission spectroscopy
Santa Maria	280	130								Emission spectroscopy
Santa Maria Valley	207	97								Emission spectroscopy
Santa Maria Valley	240	--								X-ray fluorescence (int. std.)
Santa Maria Valley	280	--								X-ray fluorescence (int. std.)
Santa Maria Valley	174	124	1.7	<1	1.7	<1	4.0	nd		Emission spectroscopy
Signal Hill	28	--								(1)
Signal Hill	25	57								Emission spectroscopy
Tejon Hills	64	44								Emission spectroscopy
Ventura	42	51								Emission spectroscopy
Ventura	49	33	33							Colorimetric
Ventura Avenue	25.2	--								(1)
Wheeler Ridge	7	2.9								Emission spectroscopy
Wilmington	43	61								Emission spectroscopy
Wilmington	41	46	28							Colorimetric
Wilmington	53	51								Emission spectroscopy
Wilmington	--	53								X-ray fluorescence (int. std.)
Wilmington	--	60								X-ray fluorescence (int. std.)
Wilmington	46	60								Emission spectroscopy
Wilmington	30	84	36	3.6	<1	nd	1	nd		Emission spectroscopy
COLORADO										
Badger Creek	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy
Badger Creek	<1	<1	<1	<1	nd	<1	<1	<1		Emission spectroscopy
Gramps	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy
Gramp	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy
Hiawatha	<1	<1	<1	<1	<1	<1	nd	<1		Emission spectroscopy
Moffat Dome	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy
Rangely	2.7	<1	<1	<1	<1	<1	nd	<1		Emission spectroscopy
Rangely	<1	<1	6.6	<1	<1	<1	<1	<1		Emission spectroscopy
Rangely	<1	<1	2.7	<1	<1	<1	<1	<1		Emission spectroscopy
Seep	0.24	4.70								Emission spectroscopy
White River Area	<1	<1	96.0	<1	<1	2.7	nd	2.2		Emission spectroscopy
FLORIDA										
Jay	nd	1								Emission spectroscopy
ILLINOIS										
Loudon	1.22	0.62	0.57							Emission spectroscopy
Loudon	0.56	--								(1)
KANSAS										
Brewster	2.1	1.3	<1	<1	<1	nd	nd	nd		Emission spectroscopy
Brewster	<1	3.9	<1	<1	<1	<1	nd	nd		Emission spectroscopy
Brock	1	2.4	10.2	<1	<1	<1	<1	nd		Emission spectroscopy
Coffeyville	3.8	1.2	7.2	<1	<1	<1	<1	<1		Emission spectroscopy
Cunningham	44.2	9.9	<1	<1	<1	<1	nd	nd		Emission spectroscopy
Cunningham	24.0	24.0	<1	<1	<1	<1	nd	nd		Emission spectroscopy
Iola	15.6	9.0	3.9	2	<1	<1	nd	nd		Emission spectroscopy
Iola	4.5	4.5	<1	<1	<1	<1	nd	nd		Emission spectroscopy
"Kansas-1"	--	>5							<.021	Emission spectroscopy
"Kansas-2"	--	>21							<.08	Emission spectroscopy
McLouth	<1	6.3	<1	<1	<1	<1	<1	nd		Emission spectroscopy
Otis Albert	21.3	6.0	<1	<1	<1	<1	nd	nd		Emission spectroscopy
Otis Albert	39.0	9.1	9.1	<1	<1	<1	<1	<1		Emission spectroscopy
Pawnee Rock	12.3	3.4	<1	<1	<1	<1	nd	nd		Emission spectroscopy
Rhodes	145	--								X-ray fluorescence (int. std.)
Rhodes	165	--								Emission spectroscopy
Rhodes	133	--								X-ray fluorescence (int. std.)
Rhodes	--	36								X-ray fluorescence (int. std.)
Rhodes	--	38								Emission spectroscopy
Rhodes	--	32								X-ray fluorescence (int. std.)
Solomon	30	7	<1	<1	<1	<1	nd	nd		Emission spectroscopy

(1) Not specified
nd Sought but not detected

TABLE A-2 (Cont'd)

State and Field	Trace Elements, ppm V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	As	Analytical Method
LOUISIANA										
Bay Hatchard	nd	2								Emission spectroscopy
Colquitt, Claiborne	nd	nd								Emission spectroscopy
Colquitt, Claiborne	nd	nd								Emission spectroscopy
Colquitt, Claiborne (Smackover B)	nd	nd								Emission spectroscopy
Delta (West) Offshore, Block 117	nd	2								Emission spectroscopy
Delta (West) Block 27	nd	2								Emission spectroscopy
Delta (West) Block 41	nd	2								Emission spectroscopy
Eugene Island, Offshore, Block 276	4	nd								Emission spectroscopy
Eugene Island, Offshore, Block 238	nd	nd								Emission spectroscopy
Lake Washington	nd	4								Emission spectroscopy
Main Pass, Block 6	nd	3								Emission spectroscopy
Main Pass, Block 41	nd	1								Emission spectroscopy
Olla	<1	5.56	0.07							Emission spectroscopy
Ship Shoal, Offshore, Block 176	nd	nd								Emission spectroscopy
Ship Shoal, Offshore, Block 176	nd	nd								Emission spectroscopy
Ship Shoal, Block 208	nd	2								Emission spectroscopy
Shongaloo, N. Red Rock	nd	nd								Emission spectroscopy
South Pass, Offshore, Block 62	nd	4								Emission spectroscopy
Timbalier, S., Offshore, Block 54	nd	nd								Emission spectroscopy
MICHIGAN										
Trent	--	0.23	[1]							Emission spectroscopy
MISSISSIPPI										
Baxterville, Lamar and Marion	40	15								Emission spectroscopy
Heidelberg	15.35	6.02	1.78							Emission spectroscopy
Mississippi	--	.7							<.003	Emission spectroscopy
Tallhalla Creek, Smith	nd	nd								Emission spectroscopy
Tallhalla Creek, Smith	nd	nd								Emission spectroscopy
Tallhalla Creek, Smith (Smackover)	nd	nd								Emission spectroscopy
Tingley, Yazoo	7	5								Emission spectroscopy
MONTANA										
Bell Creek	nd	2								Emission spectroscopy
Big Wall	24	13.2		<1	<1	<1	<1	nd		Emission spectroscopy
Soap Creek	132	13.2		<1	<1	<1	<1	nd		Emission spectroscopy
NEW MEXICO										
Rattlesnake	<1	<1	<1	<1	<1	<1	<1	nd		Emission spectroscopy
Rattlesnake	<1	<1	<1	<1	<1	<1	<1	nd		Emission spectroscopy
Table Mesa	<1	<1	9.9	<1	<1	<1	<1	<1		Emission spectroscopy
OKLAHOMA										
Allurve (Nowata)	<1	<1	1.4	6.0	<1	<1	<1	<1		Emission spectroscopy
Allurve (Nowata)	1.1	1.2	51.0	11.9	<1	<1	nd	<1		Emission spectroscopy
Allurve (Nowata)	<1	6.0	1.4	6.0	<1	<1	<1	<1		Emission spectroscopy
Bethel	--	0.11								Emission spectroscopy
Burbank	nd	nd								Emission spectroscopy
Cary	0.15	0.65								Emission spectroscopy
Chelsea (Nowata)	1.4	1.4	27.0	6.3	<1	<1	nd	nd		Emission Spectroscopy
Chelsea (Nowata)	<1	<1	6.0	<1	<1	<1	<1	<1		Emission Spectroscopy
Chelsea (Nowata)	<1	<1	<1	3.0	<1	<1	nd	<1		Emission Spectroscopy
Cheyarha	0.32	0.70								Emission spectroscopy
Cheyarha	0.34	0.95								Emission spectroscopy
Cheyarha	0.21	0.36								Emission spectroscopy
Cheyarha	0.36	4.10								Emission spectroscopy
Cromwell	0.23	0.80								Emission spectroscopy
Cromwell	0.11	0.23								Emission spectroscopy
Cromwell	0.10	0.23								Emission spectroscopy
Cromwell	--	0.27								Emission spectroscopy
Cromwell	0.10	0.42								Emission spectroscopy
Cromwell	--	0.23								Emission spectroscopy
Dill	0.23	2.10								Emission spectroscopy
Dover, Southeast	nd	nd								Emission spectroscopy
Dustin	--	0.36								Emission spectroscopy
E. Lindsay	--	0.10								Emission spectroscopy
E. Seminole	0.23	0.46								Emission spectroscopy
E. Yeager	--	0.12								Emission spectroscopy
Fish	--	0.23								Emission spectroscopy
Glen Pool	--	--	5.0							X-ray fluorescence (int. std.)

(1) Not specified

nd Sought but not detected

TABLE A-2 (Cont'd)

State and Field	Trace Element, ppm V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	Analytical Method
Grief Creek	0.10	0.42							Emission spectroscopy
Hawkins	2.10	8.50							Emission spectroscopy
Hawkins	0.72	3.50							Emission spectroscopy
Horns Corner	--	0.70							Emission spectroscopy
Katie	0.17	0.52							Emission spectroscopy
Katie	0.48	1.60							Emission spectroscopy
Katie	0.29	1.00							Emission spectroscopy
Katie	0.24	1.00							Emission spectroscopy
Kendrick	<1	<1	<1	<1	<1	<1	nd	nd	Emission spectroscopy
Konawa	0.10	0.65							Emission spectroscopy
Laffoon	44.0	20.2	1.5	<1	<1	<1	nd	nd	Emission spectroscopy
Little River	0.17	1.10							Emission spectroscopy
Middle Gilliland	<1	<1	<1	<1	<1	<1	nd	nd	Emission spectroscopy
Naval Reserve	<1	<1	<1	<1	<1	<1	nd	nd	Emission spectroscopy
New England	<1	<1	<1	nd	<1	<1	nd	nd	Emission spectroscopy
N. Dill	0.13	1.45							Emission spectroscopy
N. E. Castle Ext.	0.29	1.50							Emission spectroscopy
N. E. Elmore	0.15	0.60							Emission spectroscopy
N. E. Elmore	0.17	0.70							Emission spectroscopy
N. Okemah	0.11	0.70							Emission spectroscopy
N. W. Horns Corner	--	0.10							Emission spectroscopy
Olympia	0.88	2.40							Emission spectroscopy
Osage City	2.9	1.6	6.9	nd	<1	<1	nd	nd	Emission spectroscopy
S. W. Maysville	1.36	2.10							Emission spectroscopy
S. W. Maysville	0.25	1.10							Emission spectroscopy
Tatums	--	57							X-ray fluorescence
Tatums	--	56							Emission spectroscopy
Tatums	148	71							X-ray fluorescence (ext. std.)
Welcetka	--	0.10							Emission spectroscopy
W. Holdenville	0.13	0.46							Emission spectroscopy
W. Wewoka	0.14	0.42							Emission spectroscopy
Wewoka	--	0.15							Emission spectroscopy
Wewoka Lake	0.33	0.95							Emission spectroscopy
Wewoka Lake	0.15	0.30							Emission spectroscopy
Wewoka Lake	0.18	0.27							Emission spectroscopy
Wildhorse	2.6	1	<1	nd	nd	<1	nd	nd	Emission spectroscopy
Wynona	<1	<1	1.8	<1	<1	<1	nd	<1	Emission spectroscopy
Wynona	<1	<1	<1	<1	nd	<1	nd	<1	Emission spectroscopy
TEXAS									
Anahuac	0.2	1.1	--						Emission spectroscopy
Brantley-Jackson, Hopkins	nd	nd	--						Emission spectroscopy
Brantley-Jackson, Smackover	nd	nd	--						Emission spectroscopy
Conroe	0.008	<1	0.81						Chemical (V); emission (Ni)
East Texas	4	3	--						Emission spectroscopy
East Texas	1.2	0.88	0.51						Emission spectroscopy
East Texas	1.05	1.69	--						Colorimetric
East Texas	1.2	1.7	3.2						Colorimetric
Edgewood, Van Zandt	nd	nd	--						Emission spectroscopy
Finley	2.6	2	5.7	<1	<1	<1	<1	<1	Emission spectroscopy
Jackson	0.9	1.8	4.4						Colorimetric
Lake Trammel, Nolan			--						Emission spectroscopy
Mirando	1.4	1.9	7.6						Colorimetric
Panhandle, Carson	8	3	--						Emission spectroscopy
Panhandle, Hutchinson	6	5	--						Emission spectroscopy
Panhandle, West Texas	8.4	--	--						(1)
Refugio	0.68	0.70	0.34						Chemical
Refugio, Light	0.56	--	--						(1)
Salt Flat	8.3	3.43	1.71						Chemical
Scurry County	0.8	1.0	3.4						Colorimetric
Sweden	0.8	0.6	--						Emission spectroscopy
Talco	8.8	2.57	2.06						Chemical
Talco	6.16	--	--						(1)
Wheeler	15	nd	--						Emission spectroscopy
West Texas	23	5	--						X-ray fluoresc. spectro. (ext. std.) or emission spectroscopy
West Texas	6.7	--	--						(1)
West Texas	6.3	--	--						Emission spectroscopy
West Texas	11.8,	3.8	--						Emission spectroscopy
West Texas	8.5	4.2							Emission spectroscopy
West Texas	8.96	--	--						(1)
West Texas	7.9	4.8	5.1						Colorimetric
West Texas (Imogene)	8.5	1.73	0.88						Chemical
Yates-Pecos	7.8	2.6	0.11						Chemical

(1) Not specified

nd Sought but not detected

TABLE A-2 (Cont'd)

State and Field	Trace Element, ppm V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	Analytical Method
UTAH									
Duchesne	<1	<1	3.9	3.9	<1	<1	<1	<1	Emission spectroscopy
Duchesne	<1	<1	1.1	<1	<1	<1	<1	<1	Emission spectroscopy
Duchesne County	<1	12.7	12.1	2.9	<1	<1	nd	nd	Emission spectroscopy
Red Wash	nd	nd	--						Emission spectroscopy
Red Wash	nd	nd	--						Emission spectroscopy
Roosevelt	<1	3.7	<1	<1	<1	<1	<1	<1	Emission spectroscopy
Roosevelt	<1	5.4	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Virgin	15.4	15.4	3.4	<1	<1	<1	nd	<1	Emission spectroscopy
Virgin	8.1	8.1	1.9	<1	<1	<1	nd	<1	Emission spectroscopy
West Pleasant Valley	11.4	57	1140.0	76.6	1.1	11.4	2.7		Emission spectroscopy
Wildcat	0.14	7.5							Emission spectroscopy
WYOMING									
Beaver Creek	nd	nd							Emission spectroscopy
Big Horn Mtn	15.97	3.6	0.8						Emission spectroscopy
Bison Basin	1.1	2.7	<1	<1	<1	<1	<1	<1	Emission spectroscopy
Circle Ridge	48	31.2	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Corral Creek	59	11	--						Emission spectroscopy
Crooks Gap	2.1	2.2	1.0	<1	<1	<1	<1	<1	Emission spectroscopy
Dallas	66	15.4	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Dallas	66	66	1.5	<1	<1	<1	<1	nd	Emission spectroscopy
Derby	39	39	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Elk Basin	38	9.2	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Elk Basin	8.4	2	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Garland	35	24	3.6	<1	<1	<1	<1	nd	Emission spectroscopy
Grass Creek	106.4	28.9	1.1	<1	<1	<1	<1	nd	Emission spectroscopy
Half Moon	98.6	27.8	1.7	<1	<1	<1	<1	nd	Emission spectroscopy
Half Moon	50.6	<1	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Hamilton Dome	106.4	26.6	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Hamilton Dome	55.2	8.6	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Hamilton Dome	106.4	24.3	2.7	<1	<1	<1	<1	nd	Emission spectroscopy
Little Mo	83	16	--						Emission spectroscopy
Lost Soldier	<1	<1	<1	<1	<1	<1	<1	<1	Emission spectroscopy
Lost Soldier	<1	<1	<1	<1	<1	<1	<1	<1	Emission spectroscopy
Lost Soldier	<1	<1	<1	<1	<1	<1	<1	<1	Emission spectroscopy
Mitchell Creek	72.0	72.0	7.2	<1	<1	<1	<1	nd	Emission spectroscopy
North Oregon Basin	77.0	22.4	1.0	<1	<1	<1	<1	nd	Emission spectroscopy
North Oregon Basin	72.0	14.8	<1	<1	<1	<1	<1	nd	Emission spectroscopy
North Oregon Basin	60.0	11.5	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Oil Mountain	146.0	33.6	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Pilot Butte	45.0	10.5	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Pilot Butte	24.0	5.6	<1	<1	<1	<1	nd	nd	Emission spectroscopy
Pine Ridge	nd	nd	--						Emission spectroscopy
Prescott No. 3	21.0	7.1	--						(1)
Recluse	nd	nd	--						Emission spectroscopy
Roelfs	88	15	--						Emission spectroscopy
Salt Creek	84.0	8.4	<1	<1	<1	<1	nd	nd	Emission spectroscopy
Salt Creek	1.4	1.4	<1	<1	<1	<1	nd	nd	Emission spectroscopy
Salt Creek	<1	<1	23.4	<1	<1	<1	nd	nd	Emission spectroscopy
Salt Creek	<1	3.9	3.9	<1	<1	<1	nd	nd	Emission spectroscopy
Skull Creek	--	0.42							Emission spectroscopy
South Casper Creek	12.9	3.0	<1	<1	<1	<1	<1	nd	Emission spectroscopy
South Fork	21.9	21.9	<1	<1	<1	<1	<1	nd	Emission spectroscopy
South Spring Creek	102.0	102.0	<1	<1	<1	<1	<1	nd	Emission spectroscopy
South Spring Creek	117.0	22.3	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Steamboat Butte	29.1	6.79	<1	<1	<1	<1	<1	nd	Emission spectroscopy
Washakie	74.0	25.0	--						(1)
Winkleman Dome	48.0	11.2	1	<1	<1	<1	<1	nd	Emission spectroscopy

(1) Not specified

nd Sought but not detected.

TABLE A-3

SULFUR AND NITROGEN CONTENT OF CRUDE OILS
FROM NATIONS WHICH EXPORT TO THE U.S.

NORTH AMERICA Province and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	Production, bbl/day
Canada			
Acheson, Alta.	0.46	--	9,400
Bantry, Alta.	2.41	--	6,900
Bonnie Glen, Alta.	0.32	--	36,800
Boundary Lake, B.C.	0.72	--	27,700
Coleville, Sask.	2.62	0.126	4,700
Daly, Manitoba	0.18	--	1,400
Dollard, Sask.	2.18	--	8,800
Excelsior, Alta.	0.71	0.027	1,600
Fenn - Big Valley, Alta.	1.89	--	19,600
Fosterton-Dollard, Sask.	2.91	0.120	7,600
Gilby, Alta.	0.12	--	5,300
Golden Spike, Alta.	0.37	--	37,400
Harmattan, East, Alta.	0.37	--	6,000
Harmattan-Elkton, Alta.	0.44	--	4,500
Innisfail, Alta.	0.58	--	5,500
Joarcam, Alta.	0.13	--	5,900
Joffre, Alta.	0.56	--	6,600
Kaybob, Alta.	0.04	--	10,900
Leduc, Alta.	0.53	0.016	16,700
Lloydminster, Alta.	3.67	--	2,200
Midale, Sask.	2.24	--	11,700
North Premier, Sask.	2.92	--	6,300
Pembina, Alta.	0.22	--	140,000
Redwater, Alta.	0.22	0.041	58,000
Steelman, Sask.	0.73	--	28,200
Stettler, Alta.	1.59	0.055	3,200
Sturgeon Lake, S., Alta.	0.85	--	11,700
Swan Hills, Alta.	0.46	0.034	76,900
Taber, East, Alta.	3.08	--	4,500
Taber, West, Alta.	2.55	--	
Turner Valley, Alta.	0.34	--	2,900
Virden-Roselea, Man.	1.43	--	3,700
Virden-North Scallion, Man.	1.47	--	7,500
Wainwright, Alta.	2.60	--	10,800
Westerose, Alta.	0.25	--	9,400
West Drumheller, Alta.	0.51	--	1,900
Weybum, Sask.	1.89	--	33,300
Wizard Lake, Alta.	0.24	0.023	27,600

TABLE A-3 (cont'd)

SOUTH AMERICA Field and State	Sulfur, Weight Percent	Nitrogen, Weight Percent	Production, bbl/day
Venezuela			
Aguasay, Monagas	0.82	--	14,800
Bachaquero, Zulia	2.65	0.377	738,900
Boca, Anzoategui	0.89	0.178	6,100
Boscan, Zulia	5.54	0.593	68,400
Cabimas, Zulia	1.71	0.249	82,000
Caico Seco, Anzoategui	0.13	--	4,200
Centro del Lago, Zulia	1.42	--	132,200
Ceuta, Zulia	1.36	--	63,800
Chimire, Anzoategui	1.07	0.119	17,100
Dacion, Anzoategui	1.29	0.274	10,900
El Roble, Anzoategui	0.10	0.001	1,000
Guara, Anzoategui	2.95	0.314	26,900
Guario, Anzoategui	0.13	0.003	1,100
Inca, Anzoategui	--	0.223	9,500
La Ceibita, Anzoategui	0.41	0.055	14,300
Lago Medio, Zulia	1.16	--	58,100
Lagunillas, Zulia	2.15	0.319	940,100
Lama, Zulia	1.47	0.203	320,000
La Paz, Zulia	1.29	--	23,500
Leona, Anzoategui	1.38	--	11,900
Mapiri, Anzoategui	0.54	0.058	2,800
Mara, Zulia	1.16	0.116	10,100
Mata, Anzoategui	1.09	0.238	55,800
Mene Grande, Zulia	2.00	--	12,200
Mercy, Anzoategui	2.52	0.429	27,500
Nipa, Anzoategui	0.38	--	29,200
Oficina, Anzoategui	0.59	0.202	48,100
Oritupano, Monagas	1.89	--	14,500
Oscurote, Anzoategui	1.19	--	11,400
Pilon, Monagas	2.11	0.360	23,900
Pradera, Anzoategui	0.75	0.033	700
Quiriquire, Monagas	1.33	0.252	22,000
Ruiz, Guarico	1.05	0.161	600
San Joaquin, Anzoategui	0.14	0.036	2,300
Santa Ana, Anzoategui	0.42	--	7,000
Santa Rosa, Anzoategui	0.09	0.006	34,700
Sibucara, Zulia	0.82	0.074	2,000
Silvestre, Barinas	1.17	0.261	12,200
Sinco, Barinas	1.38	0.284	28,400
Soto, Anzoategui	0.52	0.159	10,000
Santa Barbara, Monagas	0.88	0.125	6,100
Tacat, Monagas	1.55	--	3,500
Taman, Guarico	0.14	0.025	400
Temblador, Monagas	0.83	0.338	5,300
Tia Juana, Zulia	1.70	0.269	373,000
Tucupita, Amacuro	1.05	0.312	3,700
Yopales, Anzoategui	1.15	0.275	15,700
Zapatos, Anzoategui	0.48	0.075	19,300

TABLE A-3 (cont'd)

SOUTH AMERICA (Cont'd) Country and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	Production, bbl/day
Colombia			
Casabe	1.07	--	7,500
Colorado	0.25	--	900
Galan	1.11	--	1,300
Infantas	0.88	--	4,500
La Cira	0.96	--	17,200
Payoa	0.83	0.147	8,200
Rio Zulia	0.32	--	23,700
Tibu	0.71	--	12,900
Bolivia			
Camiri	0.02	--	2,800
Chile			
Cerro Manatiales	0.05	--	--

TABLE A-3 (cont'd)

MIDDLE EAST Country and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	Production, bbl/day
Saudi Arabia and Neutral Zone			
Abqaiq	2.03	0.105	892,500
Abu Hadriya	1.69	--	103,700
Abu Sa'Fah	2.61	0.232	82,900
Berri	2.24	0.206	155,900
Dammam	1.47	--	21,600
Fadhili	1.25	0.029	47,900
Ghawar	1.89	0.107	2,057,900
Khafji	2.99	0.159	--
Khursaniya	2.53	0.093	74,300
Khurais	1.73	0.307	22,300
Manifa	2.75	0.338	5,100
Qatif	2.55	0.109	95,100
Safaniya	2.88	0.126	791,400
Wafra	3.91	0.145	141,000
Abu Dhabi			
Bu Hasa I	0.74	0.032	--
Bu Hasa II	0.77	0.031	--
Habshan	0.71	0.026	--
Murban-Bab-Bu Hasa	0.62	0.028	564,100
Iran			
Agha Jari	1.41	0.015	848,000
Cyrus	3.68	0.300	24,000
Darius	2.44	0.089	100,000
Gach Saran	1.57	0.226	882,000
Haft Kel	1.20	--	45,000
Naft-i-Shah	0.76	--	10,000
Sassan	2.06	0.082	137,000
Kuwait			
Burgan	2.58	0.122	2,950,000
Magwa-Ahmadi	2.21	0.125	
Minagish	2.12	0.103	
Raudhatain	2.13	0.102	
Sabriyah	1.82	0.096	
Iraq			
Bai Hassan	1.36	0.28	57,000
Kirkuk	1.93	--	1,097,000
Rumaila	2.1	--	480,000

TABLE A-3 (cont'd)

AFRICA

Country and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	Production, bbl/day
Nigeria			
Afam	0.09	0.027	8,400
Apara	0.11	0.050	1,000
Bomu	0.20	0.084	46,000
Delta	0.18	0.096	69,800
Ebubu	0.20	0.113	2,600
Imo River	0.20	0.121	104,100
Meji	0.15	0.041	19,400
Meren	0.09	0.048	82,700
Obagi	0.21	0.060	43,100
Oloibiri	0.26	0.179	4,200
Umuechem	0.14	0.076	32,800
Libya			
Amal	0.14	0.093	162,400
Beda	0.45	0.203	7,900
Bel Hedan	0.24	0.120	6,600
Brega*	0.22	--	
Dahra	0.41	0.106	33,300
Defa	0.28	0.140	165,800
El Dib	1.04	0.127	2,200
Es Sider*	0.42	0.160	
Farrud	0.39	0.070	4,500
Gialo	0.56	0.121	359,400
Hofra	0.32	0.082	5,200
Kotla	0.84	0.274	11,900
Nafoora	0.55	0.091	238,800
Ora	0.23	0.119	11,300
Rakb	0.23	0.118	11,500
Samah	0.25	0.127	57,000
Sarir	0.16	0.079	440,000
Umm Farud	0.13	0.033	4,200
Waha	0.24	0.134	129,300
Zaggut	0.30	0.188	2,700
Zelten	0.23	0.090	357,900

* Export crude mixture delivered to pipeline terminals.

TABLE A-3 (cont'd)

AFRICA (Cont'd)

Country and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	Production, bbl/day
Egypt			
Asl	2.05	--	*
El Alamein	0.84	0.075	24,600
El Morgan	1.67	0.183	260,900
Sudr	2.06	--	*
Angola (Cabinda)			
Tobias	1.51	--	--
Algeria			
Edjeleh	0.095	0.058	18,900
Gassi Touil	0.020	0.008	59,000
Hassi Messaoud	0.15	0.018	387,200
Ohanet	0.06	--	8,600
Rhourde el Baguel	0.31	0.087	65,900
Tin Fouye	0.13	0.061	46,200
Zarzaitine	0.06	0.018	44,200

* These fields on the Sinai Peninsula are being produced by Israel. Data are not available.

TABLE A-3 (cont'd)

ASIA

Country and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	Production, bbl/day
Indonesia			
Bekasap	0.17	0.124	111,100
Duri	0.18	0.337	37,900
Kalimantan	0.07	--	--
Lirik	0.08	--	4,500
Minas	0.115	0.132	408,700
Pematang	0.10	0.159	67,300
Seria	<.10	--	--
Tarakan	0.13	--	1,600*

* Production data from International Petroleum Encyclopedia, 1972 edition, Petroleum Publishing Co., Tulsa, Oklahoma.

TABLE A-4

TRACE ELEMENT CONTENT OF CRUDE OILS FROM NATIONS WHICH EXPORT TO THE U.S.

NORTH AMERICA

Country and Field	Trace Elements, ppm V	Ni	Fe	Cr	Analytical Method
Canada					
Acheson	0.53	1.30	0.7		Colorimetric
Acheson	3.5	1.88	2.0		Colorimetric
Acheson	0.81	4.50	0.7		Colorimetric
Armena-Camrose	0.59	0.74	0.8		Colorimetric
Bantry	56.9	19.1	1.0		Colorimetric
Bawlf	1.94	4.75	4.9		Colorimetric
Big Valley	6.83	12.3	1.1		Colorimetric
Big Valley	6.14	11.80	0.7		Colorimetric
Bonnie Glen	0.04	0.09	0.2		Colorimetric
Bonnyville	135	52.0	9.0		Colorimetric
Campbell	11.2	4.91	0.7		Colorimetric
Cantaur	86.8	33.5	1.3		Colorimetric
Cantaur	135.5	52.3	8.4		Colorimetric
Chamberlain	17.9	8.64	0.8		Colorimetric
Coleville	111	33	--		Emission spectroscopy
Coleville	13.3	5.03	4.1		Colorimetric
Coleville	105	36	0.9		X-ray fluorescence (int. std)
Coleville	95	32	--		X-ray fluorescence (ext. std)
Conrad	73.3	25.4	0.7		Colorimetric
Daly	7.04	5.26	0.8		Colorimetric
Dollard	99.7	48.5	1.7		Colorimetric
Drumheller	19.4	9.59	2.0		Colorimetric
Drumheller	4.32	13.4	0.3		Colorimetric
W. Drumheller	0.55	1.26	1.0		Colorimetric
Duhamel	0.67	7.46	0.5		Colorimetric
Duhamel	2.89	3.91	0.4		Colorimetric
Eastend	83.5	33.0	0.8		Colorimetric
Elk Island	0.7	1.66	--		Colorimetric
Excelsior	2.82	5.30	0.3		Colorimetric
Flat Lake	145	60.2	629		Colorimetric
Forget	20.8	12.74	0.3		Colorimetric
Fosterton	76.5	30.8	4.6		Colorimetric
Glen Park	0.16	1.38	0.6		Colorimetric
Golden Spike	0.37	3.63	0.7		Colorimetric
Grassy Lake	17.9	5.9	0.2		Colorimetric
Gull Lake	97.5	34.2	0.9		Colorimetric
Hamilton Lake	1.01	1.98	0.9		Colorimetric
Joffre	0.15	0.29	0.9		Colorimetric
Joseph Lake	0.48	0.55	0.3		Colorimetric
Kathyrn	4.0	2.43	16.5		Colorimetric
Lac. Ste. Anne	83.7	26.6	2.4		Colorimetric
Leduc	0.56	1.27	0.7		Colorimetric
Leduc	0.50	1.23	0.6		Colorimetric
Leduc	<0.56	--	--		(1)
Lloydminster	105	51.5	3.3		Colorimetric
Malmo	0.9	1.19	0.5		Colorimetric
Malmo	0.58	0.72	0.2		Colorimetric
Malmo	0.83	4.41	0.3		Colorimetric
Midway	90.8	40.1	1.8		Colorimetric
Morinville	105	31.1	4.2		Colorimetric
Morinville	2.21	2.75	0.8		Colorimetric
McMurray	220	75.7	75.5		Colorimetric
Pembina	0.58	1.24	0.5		Colorimetric
N. Premier	77.3	30.5	1.1		Colorimetric
Rapdan	103.1	47.5	2.1		Colorimetric
Ratcliffe	5.60	7.61	1.0		Colorimetric
Redwater	4.03	9.43	0.5		Colorimetric
Redwater	4.5	10.6	3.4		(1)
Redwater	<0.56	--	--		(1)
Roselea	4.26	2.90	0.4		Colorimetric
Skaro	0.89	2.51	--		Colorimetric
Springburn	1.24	6.24	--		Colorimetric
Smiley	1.14	2.84	1.7		Colorimetric
Stettler	11.4	15.2	0.7		Colorimetric
Stettler	16.2	13.8	0.5		Colorimetric
Success	80.0	31.6	4.1		Colorimetric
E. Taber	103	38.3	3.5		Colorimetric
W. Taber	88.8	36.3	1.0		Colorimetric
Wabiskaw	208	76.6	58.7		Colorimetric
Wagner	19.4	9.59	2.0		Colorimetric
Wapella	29.8	17.0	0.7		Colorimetric
Wapella	23.1	13.46	1.3		Colorimetric

(1) Not specified

TABLE A-4 (cont'd)

TRACE ELEMENT CONTENT OF CRUDE OILS FROM NATIONS WHICH EXPORT TO THE U.S.

SOUTH AMERICA

Country and Field ( ) *	Trace Elements, ppm V	Ni	Fe	Cr	Analytical Method
Venezuela					
Amana (1952 Blend)	29	8			Emission spectroscopy
Bachaquero	370	46			Colorimetric
Bachaquero	430	--	5.4		X-ray fluorescence
Bachaquero	430	52,38, 53			X-ray fluorescence
Bachaquero	413	49			Emission spectroscopy
Bachaquero	348	45			Emission spectroscopy
Bachaquero	320	42	3.9	0.08	(1)
Bachaquero	390	45			(1)
Bachaquero	370	46			(1)
Bachaquero	49	5.5			(1)
Bachaquero (2)	413	39			(1)
Bachaquero Light	49	5.5			Colorimetric
Bachaquero Heavy	390	45			Colorimetric
Barinas (3)	117-165	43-57			(2)
Boca	48.5	--			(1)
Boscan	1400	100			Colorimetric
Boscan	1580	123			X-ray fluorescence
Boscan	937	119			Emission spectroscopy
Boscan	819	112			Emission spectroscopy
Boscan	1200	160	60.0	1.0	(1)
Boscan	1100	105	6.2		(1)
Boscan	1150	--			(1)
Cachipo	14	3.3			(1)
Cantaura	0.6	--			(1)
Centro del Lago	179	30	32.0		(1)
Chimire	56	13			Emission spectroscopy
Cumarebo	0.7	0.8			Colorimetric
Dacion	133	29			Emission spectroscopy
Esquina	2.5	--			(1)
Esquina	1.3	--			(1)
Guanipa	110	27			Colorimetric
Guario	1.9	--			(1)
Guico (3)	17-63	--			(1)
Jusepin	26	5.5			Colorimetric
Jusepin	16.8	--			(1)
Jusepin	14.8	2.0	4.7		Emission spectroscopy
La Ceibita	0.66	--			(1)
Lagomar	179	22.0	8.4		(1)
Lagotreco	163	15			Emission spectroscopy
Lagotreco/Lagocinco	101	--			(1)
Lagunillas	290,315	--	7.9		X-ray fluorescence
Lagunillas	303	34,29 41			X-ray fluorescence
Lagunillas	303	39			X-ray fluorescence
Lagunillas	265	35.0			Emission spectroscopy
Lagunillas	236	--			(1)
Lagunillas	116	8.2	0.97		Emission spectroscopy
Lagunillas	151	--			(1)
Lagunillas	229	30			Emission spectroscopy
Lagunillas Heavy	300	38			Colorimetric
Lama	55	12			Emission spectroscopy
Lama (7)	8-26	--			(1)
Lama	104	--			(1)
Lama/Lamar	240-300	22-28			(1)
Lamar (2)	4-55	--			(1)
La Rosa	185	--			(1)
La Rosa	156	10.0	0.83		Emission spectroscopy
La Rosa Medium	230	24			Colorimetric
Leona (3)	86-140	24-36			(1)
Mapiri (3)	11-14	--			(1)
Mara	220	18			Colorimetric
Mara	206	15			Emission spectroscopy
Mara	173	16.3			(1)

* Number in parenthesis indicates number of samples involved.

(1) Not specified

TABLE A-4 (cont'd)

TRACE ELEMENT CONTENT OF CRUDE OILS FROM NATIONS WHICH EXPORT TO THE U.S.

SOUTH AMERICA (CONT'D)	Trace Elements, ppm				
Country and Field ( )[a]	V	Ni	Fe	Cr	Analytical Method
Mata, Anzoatequi	130	23			Emission spectroscopy
Mata, Anzoatequi	21	5			Emission spectroscopy
Mercy	290	64			Emission spectroscopy
Mercy (2)	242-247	31-59			(1)
Mesa (2)	45-56	22.7-25			(1)
Monagas	212	--			(1)
Motatan #7	390	43			Colorimetric
Oficina	129	--			(1)
Oficina	54	8			Emission spectroscopy
Oficina	37	6			(1)
Oficina Light	57	6			Colorimetric
Oficina Heavy	62	14			Colorimetric
Oscurote (2)	20-68	--			(1)
Oscurote, Norte	187	--			(1)
Paconsib	164	--			(1)
Pedernales	230	87			Colorimetric
Pilon	510	98			Colorimetric
Pilon	181	72			Emission spectroscopy
Quiriquire	95	16			Colorimetric
Quiriquire	102	18			Emission spectroscopy
Quiriquire	39	--			(1)
Quiriquire	31.3	5.9	2.0		Chemical
Ruiz (East)	111				(1)
San Joaquin	0.6	0.2			Colorimetric
San Joaquin	2.3	0.9			Emission spectroscopy
San Joaquin	2.4	32.0	13.1	0.024	(1)
San Joaquin	11.2	2.0			(1)
San Joaquin	0.33[b]	0.14	0.45		Chemical
San Roque	<4.5	--			(1)
Silvestre	205	63			Emission spectroscopy
Tapasito	450	40			Colorimetric
Tarra	42.0	6.6	0.49	0.009	(1)
Temblador	56	35			Colorimetric
Tia Juana	180,185	--			X-ray fluorescence
Tia Juana	182	16,20 24			X-ray fluorescence
Tia Juana	170	16			X-ray fluorescence
Tia Juana	216	24			Emission spectroscopy
Tia Juana, Light	100	11			Colorimetric
Tia Juana, Medium	200	22			Colorimetric
Tia Juana, Medium	185	--			(1)
Tia Juana, Medium	134	7.6	2.44		Chemical
Tia Juana, Heavy	300	25			Colorimetric
Tia Juana, Heavy	303	27			Emission spectroscopy
Tia Juana, Heavy	269	--			(1)
Tigre	160	28			Colorimetric
Tigre	153	31			Emission spectroscopy
Tucupita	84	45			Colorimetric
Urdaneta	430	--			Colorimetric
Zapatos	4	<1			Emission spectroscopy
Colombia					
Colombian	101	--			(1)
Casabe	135	14.4	18		(1)
Payoa	59	13			Emission spectroscopy
Tibu-Petrolea	60	9	1.6		(1)

[a] Number in parenthesis indicates number of samples involved.
(1) Not specified

TABLE A-4 (cont'd)

TRACE ELEMENT CONTENT OF CRUDE OILS FROM NATIONS WHICH EXPORT TO THE U.S.

MIDDLE EAST

Country and Field ( )*	Trace Elements, ppm V	Ni	Fe	Cr	Analytical Method
Saudi Arabia					
Abqaiq, Arab C	49	7			Emission spectroscopy
Abqaiq, Arab C	6	<1			Emission spectroscopy
Abqaiq, Arab C	<0.56	--			(1)
Abu Sa'Fah	32	12			Emission spectroscopy
Abu Sa'Fah	27	10			Emission spectroscopy
Ain Dar	51	10			Colorimetric
Ain Dar, Zone Arab D	16	3			Emission spectroscopy
Arabian Lt. (2)	11-12.4	3-3.7			(1)
Berri	24	3			Emission spectroscopy
Ghawar	17	2			Emission spectroscopy
Haradh, Zone Arab D	24	7			Emission spectroscopy
Khurais	8	5			Emission spectroscopy
Khursaniyah	18	3			Emission spectroscopy
Khursaniyah	18	<1			Emission spectroscopy
Manifa	12	1			Emission spectroscopy
Safania (3)	48-80	14			(1)
Safania, Bahrain	57	20			Emission spectroscopy
Shedgum	18	4			Emission spectroscopy
Southern Fields	16	4			Emission spectroscopy
Southern Arabian Fields	21	4			Emission spectroscopy
Uthmaniyah	51	9			(1)
Neutral Zone					
Khafji	63	12			(1)
Khafji	4	--			(1)
Wafra (2)	46-52	7			(1)
Wafra	56	--			(1)
Abu Dhabi					
Abu Dhabi (2)	nil-1.5	0.43			(1)
Abu Dhabi (Land)	1.3	--			(1)
Iran					
Agha Jari	36	--			Colorimetric
Ahwaz	23	8			(1)
Cyrus	151	39			Emission spectroscopy
Cyrus	118	--			(1)
Cach Saran	123	33			Emission spectroscopy
Cach Saran	145	31			Emission spectroscopy
Haft Kel	25	--			(1)
Iranian Heavy	107	37			X-ray fluorescence
Sassan	16	3			Emission spectroscopy
Sassan	10.8	--			(1)
Kuwait					
Kuwait	29	8			X-ray fluorescence
Kuwait	27	9			X-ray fluorescence
Kuwait	22.5	6.6	0.33		(1)
Kuwait	22.5	6.0	0.7		(1)
Magwa-Ahmadi	43	7			Emission spectroscopy
Iraq					
Ain Zalah	95	15			Colorimetric
Bai Hassan	19	--			Colorimetric
Bai Hassan	10	--			(1)
Jambur	6	--			Colorimetric
Jambur Bai Hassan	22	--			(1)
Kirkuk	30	11			Colorimetric
Kirkuk (3)	25-30	10-11			(1)
Zubair	20	4			Colorimetric
Zubair	13	--			(1)

* Number in parenthesis indicates number of samples involved.
(1) Not specified

TABLE A-4 (cont'd)

TRACE ELEMENT CONTENT OF CRUDE OILS FROM NATIONS WHICH EXPORT TO THE U.S.

Country and Field ( )*	Trace Elements, ppm V	Ni	Fe	Cr	Analytical Method
AFRICA					
Nigeria					
Afam, E. Region	<1	<1			Emission spectroscopy
Apara, E. Region	<1	1			Emission spectroscopy
Bomu, E. Region	<1	2			Emission spectroscopy
Delta, Offshore	<1	4			Emission spectroscopy
Ebuba, E. Region	<1	5			Emission spectroscopy
Imo River, E. Region	4	9			Emission spectroscopy
Imo River, E. Region	2	3			Emission spectroscopy
Kanuskiri, E. Region	<1	5			Emission spectroscopy
Kanuskiri, E. Region	<1	6			Emission spectroscopy
Ke, E. Region	<1	<1			Emission spectroscopy
Meren, Offshore	<1	<1			Emission spectroscopy
"Nigerian Medium"	7	<0.8			X-ray fluorescence
Olibiri, E. Region	2	13			Emission spectroscopy
Robert Kiri, E. Region	1	2			Emission spectroscopy
Tubu, Offshore	<1	<1			Emission spectroscopy
Umuechem, E. Region	<1	3			Emission spectroscopy
Libya					
Amal, Cyrenaica	<1	<1			Emission spectroscopy
Dalira, Concession 32	<1	3			Emission spectroscopy
Dalira, Tripolitania	<1	2			Emission spectroscopy
Dahra	0.6	--			(1)
Defa, Cyrenaica	<1	6			Emission spectroscopy
Ed Dib, Tripolitania	7	11			Emission spectroscopy
Ed Dib, Tripolitania	7	15			Emission spectroscopy
El Sider (2)	0.92-1.8	5-5.6			(1)
F-90, Concession 90	<1	<1			Emission spectroscopy
Facha, Tripolitania	4	7			Emission spectroscopy
Farud, Tripolitania	<1	4			Emission spectroscopy
Khuff, Cyrenaica	6	12			Emission spectroscopy
Kotla, Concession 47	28	35			Emission spectroscopy
Ora, Cyrenaica	<1	<1			Emission spectroscopy
Ora, Cyrenaica	<1	6			Emission spectroscopy
Rakb, Cyrenaica	<1	6			Emission spectroscopy
Sarir, Concession 65	<1	5			Emission spectroscopy
Sarir, Concession 65	<1	2			Emission spectroscopy
Sarir	<.5	5			X-ray fluorescence
Umm Farud, Conces. 92	<1	<1			Emission spectroscopy
Zelten	1.1	—			(1)
Zueitina	0.7	--			(1)
Egypt					
Belayim	23	—			(1)
Belayim	120	71.9	58		(1)
El Alamein	15	7			Emission spectroscopy
El Morgan	52	18			Emission spectroscopy
El Morgan	37	24			(1)
Algeria					
Gassi Touil	<1	<1			Emission spectroscopy
Rourde el Baquel	<1	<1			Emission spectroscopy
Zarzaitine	<1	<1			X-ray fluorescence
Zarazaitine (2)	0.2-1.5	--			(1)
ASIA					
Indonesia					
Bekasap	--	8			Emission spectroscopy
Duri	--	33			Emission spectroscopy
Minas	--	7			Emission spectroscopy
Pematang	—	11			Emission spectroscopy

* Number in parenthesis indicates number of samples involved.

(1) Not specified

TABLE A-5

TRACE ELEMENT CONTENT OF CRUDE OILS
AS DETERMINED BY ACTIVATION ANALYSIS

Region	State/Country and Field	Sulfur, Weight Percent	ppm							
			V	Ni	As	Sb	Ba	Mn	Mo	Sn
NORTH AMERICA	California, Wilmington	1.10	48.0	77.0	<.007	<.01	<.06	0.018	<.15	<.6
	Louisiana, Timbalier	0.36	1.0	<4.4	0.05	<.009	0.09	0.027	<.16	0.5
	Texas, East Texas	0.29	0.79	<3.7	<.007	<.01	<.06	0.15	<.16	<.4
	Texas, Goldsmith	1.60	5.0	<4.1	<.01	<.01	<.06	0.033	<.19	<.6
	Texas, Headlee	0.07	<.02	<2.8	<.004	0.017	<.06	<.001	<.1	<1.0
	Texas, Kelly-Snyder	0.28	0.6	<2.4	<.006	<.007	<.05	0.008	<.12	<.6
	Texas, Sprayberry	0.12	0.2	<3.9	<.01	<.01	0.6	0.026	<.18	<1.2
	Texas, Ward Estes N.	1.30	5.0	<2.6	0.7	<.008	<.04	0.06	<.13	2.4
SOUTH AMERICA	Venezuela, Ceuta	0.22	140.0	21.0	0.018	<.006	<.5	0.044	<.13	<.6
	Venezuela, Mesa	1.10	53.0	14.0	<.006	<.006	<.06	0.044	<.12	<.7
	Colombia, Orito	0.40	24.0	21.0	<.006	<.006	.08	0.006	<.12	1.5
MIDDLE EAST	Iran, Agha Jari	1.10	39.0	21.0	<.005	<.006	<.06	0.024	<.12	<.9
	Arabian Light (blend)	1.50	14.0	<9.6	<.008	<.01	<.09	0.012	<.16	<.4
	Kuwait Blend	2.90	29.0	9.0	<.005	0.8	<.5	0.005	<.14	<1.0
	Kuwait Blend	1.80	26.0	11.0	<.006	<.005	0.9	0.014	<.13	<1.4
	Middle East Blend	2.20	60.0	32.0	<.007	0.8	<.07	0.01	1.5	<1.2
AFRICA	Egypt, El Morgan	1.30	48.0	36.0	<.008	0.002	0.12	0.029	<.16	<.5
	Libya, Sarir	0.17	0.28	<4.0	<.008	<.008	<.06	0.05	<.13	<.5
ASIA	Indonesia, Duri	0.280	1.3	47.0	0.09	0.7	<.06	0.044	<.11	<.8
	Indonesia, Minas	0.06	0.1	16.0	<.01	<.007	<.07	0.006	<.11	<.8

TABLE A-5 (cont'd)

Region	State/Country and Field	Sulfur, Weight Percent	ppm V	Ni	As	Ba	Mn
NORTH AMERICA	Alaska, Nikiski	nd	62.3	79.5	0.037	0.3	6.39
	Alaska, Nikiski	0.13	0.358	nd	0.013	nd	0.026
	Alaska	2.00	0.447	nd	0.0006	0.047	0.023
	California, Wilmington	3.34	52	58.0	0.26	nd	0.045
	California	3.04	93.6	58.0	0.147	nd	2.11
	California	3.00	89.5	55.7	0.147	nd	2.47
	Louisiana, South Fields	0.38	0.778	nd	0.058	nd	0.249
	Texas, Clam Lake	0.227	0.22	3.04	0.106	0.078	0.019
	Texas, High Island	0.09	0.076	nd	0.031	0.104	0.043
	Texas, Smithbluff	0.147	0.058	nd	0.091	0.059	0.033
SOUTH AMERICA	Bolivia	0.031	0.0058	nd	nd	nd	nd
MIDDLE EAST	Abu Dhabi, Murban	1.01	0.118	nd	nd	nd	0.046
	Iran	2.40	40.9	13.6	nd	nd	0.021
AFRICA	Nigeria	0.21	0.435	nd	0.15	nd	1.29
ASIA	Indonesia, Katapa	0.0522	0.032	nd	0.042	nd	0.0053
	Indonesia, Katapa	0.061	0.0218	nd	0.074	nd	0.011

nd = not detected

TABLE A-5 (cont'd)

Region	State/Country and Field	Sulfur, Weight Percent	ppm					ppb			
			V	Ni	Fe	Mn	Se	Cr	Sb	As	Hg
NORTH AMERICA	California	1.590	100.6	199.0	79.65	1.31	0.765	12.34	44.035	516.9	114.0
	California	1.395	167.6	217.0	26.53	1.13	0.690	8.06	38.20	91.8	81.4
	California	0.920	4.0	137.5	16.84	1.01	0.151	7.87	51.13	62.9	88.2
	California	0.977	17.5	264.1	85.53	2.54	0.395	17.473	49.715	1112.4	29688.0
	California	2.387	121.5	152.9	59.51	0.73	1.396	9.144	68.8	111.7	77.83
	Louisiana	0.082	105.0	344.5	3.736	0.63	0.026	1.565	29.51	46.4	22.54
	Wyoming	2.467	298.5	112.9	5.78	0.91	0.321	8.715	71.75	111.1	76.75
AFRICA	Libya	0.469	8.2	49.1	4.938	0.79	1.096	2.302	55.2	77.3	2077.8
	Libya	1.203	7.6	76.5	120.84	1.15	0.236	15.280	106.8	151.7	62.39
	Libya	1.628	46.8	104.8	3.365	1.45	0.219	1.942	38.40	343.4	75.83
NORTH AMERICA	California, Casmalia			81						0.142	
	Kansas-1			28						0.031	
	Kansas-2			48						0.056	
	Mississippi			<2						0.010	
	Texas			<2						0.005	
SOUTH AMERICA	Venezuela			<2						0.092	
MIDDLE EAST	Mid East-1			109						0.03	
	Mid East-2			22						0.021	

TABLE A-5 (cont'd)

Region	State/Country and Field	ppm	
		V	Ni
MIDDLE EAST	Iraq, Ain Zalah	75	20
	Iraq, Ain Zalah	70	--
	Iraq, Ain Zalah	102	24.5
	Iraq, Ain Zalah	109	26
	Iraq, Bai Hassan	26.5	17.2
	Iraq, Bai Hassan	29.0	--
	Iraq, Bai Hassan	48	14.5
	Iraq, Jambur	9.0	--
	Iraq, Kirkuk	26.9	19.0
	Iraq, Kirkuk	34.0	16.6
	Iraq, Kirkuk	26.3	15.3
	Iraq, Kirkuk	--	13.8
	Iraq, Kirkuk	25.5	15.9
	Iraq, Kirkuk	25.0	16.7
	Iraq, Kirkuk	25.7	17.0
	Iraq, Kirkuk	26.0	18.0
	Iraq, Kirkuk	26.5	15.8
	Iraq, Kirkuk	47	22.9
	Iraq, Kirkuk	43	20.0
	Iraq, Kirkuk	44	20.3
	Iraq, Rumaila	35.4	13.6
	Iraq, Rumaila	13.6	--
	Iraq, Rumaila	10.6	--

TABLE A-5 (cont'd)

Region	State/Country and Field	ppm V	ppm Ni
	Iraq, Zubair	57.0	19.5
	Iraq, Zubair	15.0	8.9
	Iraq, Zubair	11.7	--
	Iraq, Zubair	19.6	--
	Iraq, Zubair	1.6	<0.7
	Iraq, Zubair	2.1	--

APPENDIX B

TABULAR DATA ON COAL ASH COMPOSITIONS

TABLE B-1. CONCENTRATIONS OF TRACE ELEMENTS IN COAL[1]

Element	Concn in whole coal (ppm)	Source[a]	Analytical method[b]	% Ash
Antimony	0.6-1.5	A	NAA	6.15-18.27
	0.1-2.0	A	SSMS	-
	<1	IE	NAA	10.9-11.2
	0.2-8.9	IE	NAA	3.28-16.04
	1.2	IW	NAA	25.85
	0.9	N	NAA	11.29-15.83
	<0.2-0.6	SW	NAA	6.56-13.65
	<0.05-1.76	SW	AS	3.85-29.60
Arsenic	5.1-35.0	A	NAA	6.15-18.27
	3.0-10.0	A	SSMS	-
	3.0-59.0	A	-	-
	3.8-18.0	IE	INAA	11.2
	1.7-93	IE	NAA	3.28-16.04
	9.3	IW	NAA	25.85
	1.2-2.5	N	NAA	11.29-15.83
	0.5-1.3	SW	NAA	6.58-13.65
	<1.0-4.0	SW	AS	3.85-29.60
	5.44	Av U.S.	-	-
Barium	20-400	A	SSMS	-
	79-91	IE	INAA	10.9-11.2
	40-1600	SW	SSMS	-
Beryllium	2.0-3.1	A	-	-
	0.6-2.6	A	OES	6.15-18.27
	0.4-3.0	A	SSMS	-
	<2	IE	-	6.80-17.26
	2.5	IE	-	-
	<5	IE	SSMS	10.9-11.2
	0.5-4.0	IE	OES	3.28-16.04
	1.2	IW	OES	25.85
	0.64-2.3	IW	-	-
	1.0-1.1	N	OES	11.29-15.83
	0.12-3.9	N	-	-
	0.4	SW	SSMS	-
	0.2-1.4	SW	OES	6.56-13.65
Boron	22-55	A	-	-
	5-83	A	OES	6.15-18.27
	1-120	A	SSMS	-
	96	IE	-	-
	100-200	IE	SSMS	10.9-11.2
	12-216	IE	OES	3.28-16.04
	66	IW	OES	25.85
	84-92	N	OES	11.29-15.83
	20-216	SW	SSMS	-
	17-138	SW	OES	6.56-13.65

(continued)

TABLE B-1. (CONTINUED)

Element	Conch in whole coal (ppm)	Source	Analytical method	% Ash
Cadmium	<0.6	A	AAS	6.15-18.27
	0.04-0.7	A	SSMS	-
	30-<300	IE	-	6.80-17.26
	0.44-0.50	IE	SSMS-ID	10.9-11.2
	<0.1-65	IE	AAS	3.28-16.04
	11.0	IW	AAS	25.85
	<0.4	N	AAS	11.29-15.83
	0-0.6	SW	-	-
	<0.6	SW	AAS	6.56-13.65
	<0.01-3.0	SW	SSMS	-
Chlorine (wt %)	0.0006-0.10	A	SSMS	-
	0.15			
	0.04-0.37	A	XRF	6.15-18.27
	0.13-0.28	IE	INAA	6.80-17.26
	0.01-0.54	IE	XRF	3.28-16.04
	0.06	IW	XRF	25.85
	0.01-0.02	N	XRF	11.29-15.83
	0.001-0.003	SW	SSMS	-
	0.01-0.03	SW	XRF	6.56-13.68
Chromium	11-15	A	-	-
	8.49-10.9	A	OES	-
	10-23	A	OES	6.15-18.27
	26-400	A	SSMS	-
	≤20	IE	-	12.6-13.4
	20	IE	-	-
	21-23	IE	INAA	10.9-11.2
	4-54	IE	OES	3.28-16.04
	22	IW	OES	25.85
	5-7	N	OES	11.29-15.83
	2-8	SW	SSMS	-
	5-8	SW	OES	6.56-13.65
Cobalt	4.1-6.7	A	-	-
	2-12	A	SSMS	-
	90			
	5-33	A	OES	6.15-18.27
	3.8	IE	-	-
	3.3-5.0	IE	INAA	10.9-11.2
	2-34	IE	OES	3.28-16.04
	43	IW	OES	25.85
	2	N	OES	11.29-15.83
	1-8	SW	SSMS	-
	1-7	SW	OES	6.56-13.65

(continued)

TABLE B-1. CONTINUED)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Copper	14-17	A	-	-
	3-180	A	SSMS	-
	11-28	A	AAS/OES	6.15-18.27
	5-20	IE	-	6.8-10.9
	11	IE	-	-
	50-100	IE	SSMS-ID	10.9-11.2
	5-33	IE	AAS/OES	3.28-16.04
	61	IW	AAS/OES	25.85
	15-18	N	AAS/OES	11.29-15.83
	15	N	-	-
	1-15	SW	-	-
	10-22	SW	AAS/OES	6.56-13.65
	60-180	SW	SSMS	-
	9.6	SW	XRF	6
Fluorine	50-120	A	-	-
	1-19	A	SSMS	-
	110			
	50-125	A	ISE	6.15-18.27
	50-100	IE	-	-
	30-143	IE	ISE	3.28-16.04
	65-120	IW	-	-
	91	IW	ISE	25.85
	60-70	N	-	-
	42-52	N	ISE	11.29-15.83
	8	SW	SSMS	-
	39-105	SW	ISE	6.56-13.68
	<50.0-220.0	SW	ISE	3.85-29.60
Lead	4-14	A	-	-
	4-18	A	AAS/OES	6.15-18.27
	2-36	A	SSMS	-
	8-14	IE	-	-
	7.4	IE	SSMS-ID	10.9-11.2
	4-218	IE	AAS/OES	3.28-16.04
	102	IW	AAS/OES	25.85
	4	IW	-	-
	7	N	AAS/OES	11.29-15.83
	7	N	-	-
	1-2	SW	SSMS	-
	4-7	SW	AAS/OES	6.56-13.65
Manganese	5-48	A	SSMS	-
	9-55	A	NAA	6.15-18.27
	25-95	IE	-	6.8-17.26
	51-54	IE	INAA	10.9-11.2
	6-181	IE	NAA	3.28-16.04
	108	IW	NAA	25.85
	88-101	N	NAA	11.29-15.83

(continued)

TABLE B-1. (CONTINUED)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Manganese (Cont.)	6-22	SW	NAA	6.56-13.68
	10-240	SW	SSMS	-
	5-200	-	OES	-
Mercury	0.12-0.21	A	-	-
	<0.3-0.5	A	SSMS	-
	0.08-0.46	A	NAA	6.15-18.27
	0.16-1.91	IE	-	6.80-17.26
	0.13	IE	-	-
	0.170-0.063	IE	FAAS	10.9-11.2
	0.04-1.60	IE	NAA	3.28-16.04
	0.19	IW	-	-
	0.18	IW	NAA	25.85
	0.07	N	-	-
	0.07-0.09	N	NAA	11.29-15.83
	0.11-0.74	SE	FAAS	10.63-18.58
	0.02-0.06	SW	NAA	6.56-13.68
	<0.3	SW	SSMS	-
	0.02-1.20	SW	FAAS	3.85-29.60
	0.07	SW	FAAS	6
	0.05-0.38	-	NAA/AAS	-
Molybdenum	1.5-5.8	A	-	-
	1-5	A	SSMS	-
	10			
	1-11	A	OES	6.15-18.27
	4.3	IE	-	-
	10-20	IE	SSMS	10.9-11.2
	<1-29	IE	OES	3.28-16.04
	2.6-4.3	IW	-	-
	14	IW	OES	25.85
	8-30	N	OES	11.29-15.83
	<1-2	SW	OES	6.56-13.68
	1-4	SW	SSMS	-
	0.99	SW	XRF/WC	-
Nickel	9.7-20.0	A	-	-
	3-60	A	SSMS	-
	11-22	A	XRF/OES/AAS	6.15-18.27
	<20-90	IE	-	6.8-10.9
	15	IE	-	-
	8-68	IE	XRF/OES/AAS	3.28-16.04
	80	IW	XRF/OES/AAS	25.85
	11-24	IW	-	-
	4-6	N	XRF/OES/AAS	11.29-15.83
	4	SW	SSMS	-
	3-8	SW	XRF/OES/AAS	6.56-13.68
	10-30	SW	OES	-

(continued)

TABLE B-1. (CONTINUED)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Selenium	0.04-0.3	A	SSMS	-
	1.3-6.6	A	NAA	6.15-18.27
	2.6-3.4	IE	INAA	10.9-11.2
	0.4-7.7	IE	NAA	3.28-16.04
	2.9	IW	NAA	25.85
	0.8	N	NAA	11.29-15.83
	0.5-3.9	SW	-	-
	1.2-2.3	SW	NAA	6.58-13.68
	0.40-3.90	SW	XRF	3.85-29.60
	1.9	SW	XRF	6
Tellurium	<0.1-0.4	A	SSMS	-
	1-3	IE	SSMS	10.9-11.2
	0.2	SW	SSMS	-
	<0.02-0.10	SW	WC	3.85-29.60
Thallium	2-36	A	SSMS	-
	2.4-3	IE	INAA	10.9-11.2
	<0.20-1.40	SW	AAS	3.85-29.60
Tin	0.1-0.9	A	-	-
	1-47	A	SSMS	-
	<3-8	A	OES	6.15-18.27
	1-5	IE	-	-
	20	IE	SSMS	10.9-11.2
	<1-51	IE	OES	3.28-16.04
	<10	IW	OES	25.85
	0.6-1.6	IW	-	-
	<5-15	N	OES	11.29-15.83
	4-35	SW	SSMS	-
	<2-8	SW	OES	6.56-13.68
Titanium (wt %)	0.02-0.18	A	SSMS	-
	0.06-0.15	A	XRF	6.15-18.27
	0.05-0.17	IE	-	6.8-17.26
	0.07	IE	NAA	10.9
	0.02-0.15	IE	XRF	3.28-16.04
	0.08	IW	XRF	25.85
	0.06	N	XRF	11.29-15.83
	0.05-0.09	SW	SSMS	-
	0.03-0.13	SW	XRF	6.56-13.68
Uranium	0.3-1.0	A	SSMS	-
	0.09-3.70	SW	INAA	3.85-29.60

(continued)

TABLE B-1. (CONTINUED)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Vanadium	19-25	A	-	-
	3-77	A	SSMS	-
	24-52	A	XRF/OES	6.15-18.27
	35	IE	-	-
	21-69	IE	INAA	10.9-11.2
	16-78	IE	XRF/OES	3.28-16.04
	40	IW	XRF/OES	25.85
	14-18	N	XRF/OES	11.29-15.83
	11-26	SW	XRF/OES	6.56-13.68
	2-8	SW	SSMS	-
	10-22.5	-	OES	-
	17-22	IW	-	-
Zinc	4.4-12	A	-	-
	3-80	A	SSMS	-
	21-40	A	AAS	6.15-18.27
	118-<3000	IE	-	6.8-17.26
	44	IE	-	-
	85-250	IE	SSMS	10.9-11.2
	10-5350	IE	AAS	3.28-16.04
	22-53	IW	-	-
	1444	IW	AAS	25.85
	59	N	-	-
	10-12	N	AAS	11.29-15.83
	1-17	SW	-	-
	4-26	SW	SSMS	-
	7-15	SW	AAS	6.56-13.68
	7.3	SW	XRF	6

a. Abbreviations for coal sources

A = Appalachian (Pennsylvania, Maryland, Virginia, West Virginia, Ohio, Eastern Kentucky, Tennessee, Alabama).

Av U.S. = A representative average for U.S. coals.

IE = Interior Eastern (Illinois, Indiana, Western Kentucky).

IW = Interior Western (Iowa, Missouri, Kansas, Oklahoma, Arkansas).

N = Northern Plains (Montana, North and South Dakota).

SW = Southwestern (Arizona, New Mexico, Colorado, Utah).

(continued)

TABLE B-1. (CONTINUED)

b. Abbreviations for analytical methods

AAS	=	Atomic Absorption Spectroscopy
AS	=	Absorption Spectroscopy
FAAS	=	Flameless Atomic Absorption Spectroscopy
GC-MES	=	Gas Chromatography with Microwave Emission Spectroscopic Detection
INAA	=	Instrumental Neutron Activation Analysis
ISE	=	Ion-Selective Electrodes
NAA	=	Neutron Activation with Radiochemical Separation
OES	=	Optical Emission Spectroscopy-Detection Method Unspecified
OES-DR	=	Optical Emission Spectroscopy with Direct Reading Detection
OES-P	=	Optical Emission Spectroscopy with Photographic Detection
PAA	=	Photon Activation Analysis
PES	=	Plasma Emission Spectroscopy
SSMS	=	Spark Source Mass Spectroscopy
SSMS-ID	=	Spark Source Mass Spectroscopy with Isotope Dilution
WC	=	Wet Chemistry
XRF	=	X-Ray Fluorescence Spectroscopy

TABLE B-2. QUANTITATIVE ANALYSES (in ppm) FOR 13 TRACE ELEMENTS IN DRILL-CORE COAL SAMPLES, POWDER RIVER BASIN(2)

Sample interval (ft)	Drill-core sample no.	ppm, ash					Ash, %
		Cd	Cu	Li	Pb	Zn	
100-109	458	-	335	27	-	185	3.20
109-112	459	1.5	385	130	275	180	6.80
240-247	462	<1.0	420	50	545	175	3.25
231-232	463	<1.0	605	93	1660	195	4.56
116-127	464	<1.0	245	31	300	83	4.56
127-137	465	<1.0	180	28	195	93	3.43
137-140	466	1.5	145	44	120	240	7.12
100-104	467	<1.0	100	50	100	185	6.92
60-68	468	1.5	130	43	105	350	8.16
166-176	469	<1.0	120	27	80	115	4.87
108-118	470	<1.0	140	33	140	72	8.08
216-226	471	1.0	224	34	420	100	7.30
71-72	472	1.0	316	16	220	160	6.42
80-88	473	<1.0	80	20	110	24	8.24
88-98	474	<1.0	90	11	130	32	5.40
143-150	475	<1.0	180	21	120	42	6.20
92-101	476	1.5	180	57	87	480	11.3
101-106	477	<1.0	105	27	100	122	5.67
140-147	478	<1.0	105	16	100	104	5.00
109-110	479	<1.0	92	45	79	232	14.8
110-120	480	<1.0	84	25	69	224	6.52

TABLE B-2. (CONTINUED)

Sample interval (ft)	Drill-core sample no.	ppm, coal							
		As	F	Hg	Sb	Se	Te	Tl	U
100-109	458	2.	40	0.035	0.92	<0.1	0.1	<0.2	<0.2
109-112	459	2.	30	0.082	0.62	0.4	0.1	<0.2	0.8
240-247	462	2.	10	0.037	0.08	<0.1	<0.02	<0.2	<0.2
231-232	463	3.	10	0.051	0.12	<0.1	0.02	<0.2	0.4
116-127	464	1.	30	0.044	0.04	0.2	<0.02	<0.2	<0.2
127-137	465	1.	20	0.030	0.04	<0.1	<0.02	<0.2	<0.2
137-140	466	3.	30	0.106	0.06	0.6	<0.02	<0.2	1.2
100-104	467	2.	30	0.035	0.08	<0.1	<0.02	<0.2	0.9
60-68	468	2.	60	0.049	0.04	0.5	0.1	<0.2	0.8
166-176	469	2.	10	0.099	<0.04	0.2	0.05	<0.2	<0.2
108-118	470	3.		0.043		0.6			0.9
216-226	471	4.		0.065		0.5			0.3
71-72	472	5.		0.039		0.9			0.5
80-88	473	3.		0.035		0.5			0.4
88-98	474	2.		0.021		0.3	Not determined	Not determined	<0.2
143-150	475	3.		0.058		1.0			<0.2
92-101	476	5.		0.181		1.5			1.7
101-106	477	3.		0.048		0.5			0.5
140-147	478	4.		0.028		0.6			0.3
100-110	479	4.		0.041		1.2			1.5
110-120	480	3.		0.035		0.3			0.4

TABLE B-3. TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT[3]

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Ag[b]	5	<2	<2	<3–5			<3	<0.20	<0.20–0.33			
	7			<1	~1	1			<0.07		~0.002	0.001
	9	<2–5		<2			6		<0.10			
Ag[c]	7	<10	<20	10	3	20	<13	<1.0	0.68		0.0056	0.024
Al[b]	5	1.05%	7.6%	5.7%			1.31×10^4	7.5×10^3	3.8×10^3	-14		
	7	1.3%	9.7%	7.4%	20%	38%	1.6×10^4	9.9×10^3	5.0×10^3	6.9	3.7×10^2	4.5×10^2
	9	1.06%	6.6%	6.9%	3.5%		1.3×10^4	7.2×10^3	3.4×10^3	-18	68	
Al[c]	5	0.9%	5%	5%	20%		1.1×10^4	5.0×10^3	3.3×10^3	-25	3.8×10^2	
	7	>1%	>10%	>10%	>10%	>10%	$>1.3 \times 10^4$	1.0×10^4	$>6.8 \times 10^3$		$>1.9 \times 10^2$	$>1.2 \times 10^2$
	9	1%	5%	15%	10%		1.3×10^4	5.5×10^3	7.3×10^3	-1.5	1.9×10^2	
As[b]	5	4.7	<10	27			5.9	<0.99	1.8			
	7	18		349	138	93	23		24		0.26	0.11
	9	3.8	0.5	46	50		4.7	0.05	2.2	-52	0.097	
As[c]	5	5	1	5	100		6.2	0.10	0.33	-93	0.19	
	7			1000	30	100			68		0.056	0.12
	9	5	2	40	20		6.2	0.22	2.0	-64	0.039	
B[c]	5	200	300	3000	300		250	30	200	-8	0.57	
	7	100	200	250	150	170	130	20	17	-71	0.28	0.20
	9	200	300	2000	300		250	33	97	-48	0.59	
Ba[b]	5	91		400			114		27			
	9	79	600				99	66				
Ba[c]	5	100	300	3000	300		130	30	200	77	0.57	
	7	150	500	300	150	100	190	51	20	-63	0.28	0.12
	9	100	300	1700	100		130	33	83	-11	0.19	
Be[c]	5	<5	5	15	5		<6.3	0.50	1.0		0.01	
	7	0.3	0.5	3	1	0.3	0.4	0.05	0.21	-35	0.0019	0.00036
	9	<5	<10	17	<10		<6.3	<1.1	0.83		<0.019	
Bi[c]	7	<10	<10	2	2	5	<13	<1.0	0.14		0.0037	0.0059
Br[b]	5	2.6	<1	<2–5			3.3	<0.1	<0.13–0.33			
	9	2.0	<0.5	<5	10		2.5	<0.05	<0.24		0.019	

(continued)

TABLE B-3. (CONTINUED)

Element	Run	Concentration (ppm unless otherwise indicated) Coal	S.T.	P.T.	P.O.	Stack	Mass flow (g/min) Coal	S.T.	P.T.	Imbalance (%)[a]	P.O.	Stack
Ca[b]	5	0.36%	2.06%	1.57%			0.45×10^4	2.0×10^3	1.04×10^3	-32		
	7	0.51%	4.4%	2.2%	1.2%	<1.0	0.64×10^4	4.5×10^3	1.5×10^3	6.3	22	<12
	9	0.38%	2.7%	1.4%	0.49%		0.47×10^4	3.0×10^3	6.8×10^2	22	9.5	
Ca[c]	5	1%	5%	3.5%	0.3%		1.3×10^4	5.0×10^3	2.3×10^3	-44	5.7	
	7	1%	5%	>1%	<1%	>1%	1.3×10^4	5.1×10^3	$>6.8 \times 10^2$		>19	>12
	9	0.5%	3%	3%	1%		0.6×10^4	3.3×10^3	1.5×10^3	20	19	
Ce[c]	9	<50					<37					
Cd[c]	5	0.44[d]	2	<2			0.55	0.20	<0.13			
	7			<2	<0.7	<0.7			<0.14		<0.0013	<0.00083
	9	0.50[d]	2	<10-20	7		0.63	0.22	<0.49-0.97		0.014	
Cl[b]	5	407		50			510		3.3			
	9	355		<5-50	1000		460		<0.24-2.4		1.9	
Co[b]	5	3.5	15	35			4.4	1.5	2.3	-14		
	7	5	28	51	26	11	6.3	2.9	3.5	1.6	0.048	0.013
	9	3.3	19	25	58		4.1	2.1	1.2	-19	0.11	
Co[c]	5	10					13				0.56	0.012
	7	<10	<50	50	30	10	<13	<5.1	3.4			
	9	7	40	70	40		9	4.4	3.4	-13	0.078	
Cr[b]	5	23	895				29	89				
	7		111	200				11	14			
	9	21	180	356	300		26	20	17	42	0.59	
Cr[c]	5	65	300	250	200		81	30	17	-42	0.38	
	7	150	500	170	200	150	190	51	12	67	0.37	0.18
	9	30	<200	70	40		37	<22	3.4		0.078	
Cs[b]	5	1.5	8.8	15			1.9	0.87	1.0	-1.6		
	9	1.5	8	21	4		1.9	0.88	1.02	0	0.0078	
Cu[c]	5	50	300	300	200		63	30	20	-21	0.38	
	7	100	200	400	400	1000	130	20	27	-64	0.74	1.2
	9	50	200	400	400		63	22	19	-35	0.78	
Dy[c]	9	<10					<13					
Eu[b]	5	0.31	0.7	1.6			0.40	0.07	0.11	-55		
	9	0.17	1.4	1.8			0.21	0.15	0.09	14		

TABLE B-3. (CONTINUED)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T	P.I.	Imbalance (%)[a]	P.O.	Stack
Eu[c]	9	~1					~1.3					
Fe[b]	5	1.46%	10.3%	9.5%			1.83×10^4	1.0×10^4	6.3×10^3	-11		
	7	2.0%	13.2%	13.9%	9.6%	4.0%	2.5×10^4	1.4×10^4	9.5×10^3	-6.0	1.8×10^2	4.8×10^1
	9	1.3%	10.1%	9.3%	23.5%		1.6×10^4	1.1×10^4	4.5×10^3	-3.1	4.6×10^2	
Fe[c]	5	2%	10%	10%	10%		2.5×10^4	9.9×10^3	6.6×10^3	-34	1.9×10^2	
	7	~2%	~8%	>2%	>2%	>2%	$\sim 2.5 \times 10^4$	$\sim 8.2 \times 10^3$	$>1.4 \times 10^3$		$>3.7 \times 10^1$	$>2.4 \times 10^1$
	9	2%	10%	10%	10%		2.5×10^4	1.0×10^4	4.9×10^3	-40	1.9×10^2	
Ga[b]	7			71	93	130			4.8		0.17	0.15
Ga[c]	5		40	100	100			4.0	6.6		0.19	
	9	13	<10	70	40		16	<1.1	3.4		0.078	
Ge[c]	5	15	2	200	200		19	0.20	13	-31	0.38	
	9	5	<10	70	40		6.3	<1.1	3.4		0.078	
Hf[b]	5	4.4					5.5					
	9	3.0					3.7					
Hg[c]	5			0.11[d]	<1				0.007[d]		<0.0019	
	9			0.13[d]	~10				0.006[d]		~0.019	
Hg[e]	5	0.064	0.07	0.04			0.080	0.0069	0.0027	-88		
	7	0.170		0.10			0.212		0.007			
	9	0.063	0.09	0.043			0.079	0.0099	0.0021	-85		
K[b]	5	0.20%	1.14%	1.17%			0.25×10^4	1.1×10^3	7.8×10^2	-25		
	7	0.25%	1.46%	1.97%	0.88%	0.29%	0.31×10^4	1.5×10^3	1.3×10^3	-9.7	16	3.5
	9	0.22%	0.95%	1.65%	1.28%		0.27×10^4	1.0×10^3	8.0×10^2	-33	25	
K[c]	5	0.17%	1.5%	1.7%	0.3%		0.21×10^4	1.5×10^3	1.1×10^3	24	5.7	
	7	0.1%	3%	1%	0.5%	0.05%	0.13×10^4	3.1×10^3	6.8×10^2	190	9.3	0.6
	9	0.06%	0.5%	0.7%	0.2%		0.07×10^4	5.5×10^2	3.4×10^2	27	3.9	
La[b]	5	4.8	35	30			6.0	3.5	2.0	-8.3		
	7	6	46	36	19	12	7.5	4.7	2.46	-4.5	0.035	0.014
	9	5.0	42	32			6.3	4.6	1.5	-3.2		
La[c]	9	~10					~13					
Li[c]	5	30	300	350	70		37	30	23	43	0.13	
	7	100	500	200	100	50	130	51	14	-50	0.19	0.059
	9	25	200	300	200		31	22	15	19	0.39	

TABLE B-3. (CONTINUED)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Mg[b]	5	0.15%	0.98%	0.89%			0.18×10^4	9.7×10^2	5.9×10^2	-13		
	7	0.17%	1.3%	1.16%		2.5%	0.21×10^4	1.3×10^3	7.9×10^2	-0.4		30
	9	0.17%	0.41%	0.55%	0.88%		0.21×10^4	4.5×10^2	2.7×10^2	66	17	
Mg[c]	5	0.15%	0.6%	1%	0.8%		0.18×10^4	5.9×10^2	6.6×10^2	31	15	
	7	0.1%	0.5%	>1%	0.7%	1%	0.12×10^4	5.1×10^2	$>6.8 \times 10^2$		13	12
	9	0.15%	0.7%	0.7%	0.4%		0.18×10^4	7.7×10^2	3.4×10^2	-38	7.8	
Mn[b]	5	53	416	325			66	41	22	-4.5		
	7	51	382	316	335	218	64	39	21	6.3	0.62	0.26
	9	54	418	323	550		67	46	16	7.5	1.1	
Mn[c]	5	100	1000	1000	1000		130	99	66	27	1.9	
	7	200	700	1000	500	900	250	72	68	-44	0.93	1.1
	9	100	1000	700	500		130	110	34	11	0.97	
Mo[b]	5	47					59					
	9	20					25					
Mo[c]	5	20	100	150	200		25	9.9	10	-20	0.38	
	7	10	70	700	150	70	12	7.2	48	360	0.28	0.083
	9	20	80	200	20		25	8.8	9.7	-26	0.039	
Na[b]	5	0.063 - 0.63%	0.33%	0.59%			790 - 7900	3.3×10^3	3.9×10^2			
	7	0.072%	0.29%	0.58%	0.40%	0.33%	900	3.0×10^2	4.0×10^2	-22	7.4	3.9
	9	0.069%	0.32%	0.7%	0.28%		860	3.5×10^2	3.4×10^2	-20	5.5	
Na[c]	5	0.05%	0.3%	0.5%	0.15%		630	3.0×10^2	3.3×10^2	0	2.85	
	7	0.15%	0.3%	>1%	0.3%	0.09%	0.19×10^9	3.1×10^2	$>6.8 \times 10^2$	-48	5.6	1.1
	9	0.03%	0.2%	0.3%	0.2%		370	2.2×10^2	1.5×10^2	0.0	3.9	
Nb[c]	5	<15	2	6	20		<19	0.20	0.40		0.038	
	7	<10	<10	10	10	20	< 13	<1.0	0.68		0.019	0.024
	9	~5	2	15	10		~6.3	0.22	0.73		0.019	
Nd[c]	9	~30					~37					
Ni[c]	5	≤100	500	500	1000		≤130	50	33		1.9	
	7	150	150	1000	500	300	190	15	68	-56	0.93	0.36
	9	<100	500	500	1000		<130	55	24		1.9	
P[c]	5		60	200	200			6.0	13		0.38	
	7			300	300	200			20		0.56	0.24
	9	50	20	500	200		63	2.2	24	-58	0.39	

TABLE B-3. (CONTINUED)

Reproduced from best available copy.

Element	Run	Concentration (ppm unless otherwise indicated)					Mass Flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Pb[c]	5	≤5	3	80	800		≤6.3	0.30	5.3		1.5	
	7	~30	<10	300	100	70	~37	1.0	20		0.19	0.083
	9	<20	3	250	100		<25	0.33	12		0.19	
Rb[b]	9	~10					13					
	5	17	28	162			21	2.8	11	34		
	7	20					25					
	9	19.4	100	<120			24.3	11	<5.8			
Rb[c]	5	40	400	650	100		50	40	43	66	0.19	
	7	200		300	50	30	250		20		0.093	0.036
	9	17	40	200	10		21	4.4	9.7	-33	0.019	
S[b]	5	3.5%					4.4×10^4					
	9	5.1%			10.5%		6.4×10^4				2.0×10^2	
Sb[b]	5	<1	<0.2	3.2			<0.75	<0.02	0.2			
Sb[c]	5		8	7	10			0.79	0.47		0.019	
	7			<10	<10	<10			<0.68		<0.019	<0.012
Sc[b]	5	3.4	20	25			4.3	2.0	1.7	-14		
	7	3.6	22	29	10	5	4.5	2.3	2.0	-4.4	0.019	0.0059
	9	3.2	22	25	10		4.0	2.4	1.2	-10	0.019	
Se[b]	5	3.2	9.6	24(<60)			4.0	1.0	1.6(<4.0)			
	7	2.6		23	290	44	3.3		1.6		0.54	0.052
	9	3.2	14	<32, 48	760		4.0	1.5	<1.5-2.3		1.4	
Se[c]	9	6	20	20	200		7.5	2.2	0.97	-58	0.39	
Si[c]	5	5%	30%	30%	30%		6.3×10^4	3.0×10^4	2.0×10^4	-21	5.7×10^2	
	7	5%	>10%	>5%	>5%	>5%	6.3×10^4	$>1.0 \times 10^4$	$>3.4 \times 10^3$		>93	>59
	9	5%	30%	30%	10%		6.3×10^4	3.3×10^4	1.5×10^4	-24	1.9×10^2	
Sm[b]	5	1	0.12				1.3	0.01				
	9	1					1.3					
Sm[c]	9	~10					~13					
Sn[c]	7	20	200	20	20	20	25	20	1.4	-14	0.037	0.024
Sr[c]	7	200	500	300	100	100	250	51	20	-72	0.19	0.12
	9		60	200	60			6.6	9.7		0.12	

TABLE B-3. (CONTINUED)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Ta[b]	5	0.1, <1		1.2			0.13, <1.3		0.08			
	9	<1	2	1.3, <5			<1.3	0.22	0.06, <0.24			
Ta[c]	7	<10	200	50	20	20	<13	20	3.4		0.037	0.024
Tb[c]	9	<1					<1.3					
Te[c]	5	3	3	<1	<1		3.7	0.30	<0.07		<0.0019	
	9	1	3	~10	~10		1.3	0.33	~0.49		~0.019	
Th[b]	5	2.4		23			3.0		1.5			
	9	3	20	18			3.7	2.2	0.87	-17		
Th[c]	7			10	7	3			0.68		0.013	0.0036
Ti[b]	5	580	3300	4200			730	330	280	16		
	7	500	2400	3500	3400		630	250	240	-22	6.3	
	9	710	3000	3700	2500		890	330	180	-43	4.9	
Ti[c]	5	650	3000	~3000	2000		810	300	~200		3.8	
	7	700	3000	1500	700	1000	880	310	100	-53	1.3	1.2
	9	700	2000	5000	1000		880	220	240	-48	1.9	
Tl[c]	9	<2	2	40	30		<2.5	0.22	1.9		0.059	
	7			100	30				6.8		0.056	
U[b]	5	3	1	15			3.7	0.10	1.0	70		
	7	3.3	17	21	12.4		4.1	1.7	1.4	24	0.023	
	9	1.67	14	17	7		2.09	1.5	0.83	11	0.014	
U[c]	7			100	20	10			6.8		0.037	0.012
V[b]	5	21	135	211			26	13	14	3.8		
	7	69	560	780	406		86	57	53	28	0.75	
	9	21	125	200	63		26	14	9.7	-8.8	0.12	
V[c]	5	12	30	100	100		15	3.0	6.6	36	0.19	
	7	50	100	200	100	100	63	10	14	62	0.19	0.12
	9	30	100	350	100		37	11	17	24	0.19	
W[b]	9	<5					<6.3					
W[c]	7	<10		50	20	≤5	<13		3.4		0.037	<0.0059
	9	1	1	5	1		1.3	0.11	0.24	73	0.0019	

TABLE B-3. (CONTINUED)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Zn[c]	5	250	900	3000	9000		310	89	200	-6.8	17	
	7	<200	<200	500	500	300	<250	<20	34		0.93	0.36
	9	85	100	3000	900		110	11	150	46	1.7	
Zr[c]	5		10	10	100			1.0	0.66		0.19	
	7	40	100	100	50		50	20	6.8	-46	0.093	
	9	<30	10	40	10		<37	1.1	1.9		0.019	

[a] $\text{Imbalance} = \frac{\text{S.T.} + \text{P.I.} - \text{coal}}{\text{coal}} \times 100.$

[b] Neutron activation analysis

[c] Spark source mass spectroscopy.

[d] Isotope dilution SSMS

[e] Atomic absorption spectroscopy.

ST - Slag tank solids

PI - Precipitator Inlet Flyash

PO - Precipitator Outlet Flyash

TABLE B-4. AVERAGE TRACE ELEMENT CONTENT IN ASH OF COAL FROM THREE AREAS,[1] PERCENT[4]

Element	Crustal abundance[2]	Approximate lower limit of detection[3]	Eastern Province		Interior Province		Western States	
			Frequency of detection	Average trace element content of ash	Frequency of detection	Average trace element content of ash	Frequency of detection	Average trace element content of ash
Barium	0.0425	0.002	100	0.0876	100	0.0399	100	0.1467
Beryllium	.00028	.0001	100	.0012	100	.0014	100	.0006
Boron	.0010	.0002	100	.0265	100	.0731	100	.0529
Chromium	.0100	.0001	100	.0230	100	.0224	100	.0066
Cobalt	.0025	.0020	100	.0184	98	.0193	98	.0097
Copper	.0055	.0001	100	.0128	100	.0089	100	.0047
Gallium	.0015	.0002	100	.0071	100	.0039	100	.0033
Germanium	.00015	.0003	99	.0048	100	.0104	95	.0017
Lanthanum	.0030	.01	92	.0145	86	.0131	81	.0128
Lead	.0013	.0001	100	.0055	100	.0131	100	.0029
Lithium	.0020	.0001	100	.0584	100	.0235	100	.0168
Manganese	.0950	.0001	100	.0260	100	.0325	100	.0212
Molybdenum	.00015	.0001	99	.0082	99	.0073	100	.0020
Nickel	.0075	.0001	100	.0209	100	.0262	100	.0054
Scandium	.0022	.002	100	.0089	100	.0069	97	.0052
Strontium	.0375	.001	100	.1052	100	.0658	100	.1456
Tin	.0002	.0001	100	.0019	99	.0019	100	.0017
Vanadium	.0135	.0001	100	.0336	100	.0325	100	.0152
Ytterbium	.00034	.0001	100	.0007	100	.0005	100	.0003
Yttrium	.0033	.001	100	.0142	100	.0118	100	.0076
Zinc	.0070	.005	98	.0230	100	.0743	93	.0258
Zirconium	.0165	.005	100	.0704	100	.0825	100	.0850
Arsenic	.00018	.005	67	.0159	41	.0119	16	.0073
				(.0107)		(.0049)		(.0012)
Bismuth	.00002	.0001	82	.0002	77	.0001	83	.0001
				(.0002)		(.0001)		(.0001)
Cerium	.0060	.02	31	.0238	11	.0214	13	.0238
				(.0074)		(.0024)		(.0031)
Neodymium	.0028	.01	29	.0213	10	.0183	15	.0295
				(.0062)		(.0018)		(.0044)
Niobium (columbium)	.0020	.001	73	.0053	88	.0055	85	.0053
				(.0039)		(.0048)		(.0045)
Rubidium	.0090	.001	97	.0239	100	.0276	58	.0064
				(.0232)		(.0276)		(.0037)
Thallium	.00005	.0005	43	.0019	49	.0008	9	.0005
Average ash..pct of dry coal	-	-	-	9.3	-	10.5	-	9.8
Number of samples	-	-	-	600	-	123	-	104

[1] Averages calculated for number of samples in which element was detected, except that averages in parentheses were calculated for all of the samples tested using zero for element contents below limit of detection.

[2] Mason, Brian. Principles of Geochemistry. John Wiley & Sons, Inc., New York, 3d ed., 1966, pp. 45-46.

[3] Peterson, M. J., and J. B. Zink. A Semiquantitative Spectrochemical Method for Analysis of Coal Ash. BuMines Rept. of Inv. 6496, 1964, pp. 6-10.

TABLE B-5. AVERAGE TRACE ELEMENT CONTENT IN ASH OF COALS FROM STATES IN EASTERN PROVINCE, PERCENT OF ASH[4]

Element	Alabama	Eastern Kentucky	Maryland	Ohio	Pennsylvania	Tennessee	Virginia	West Virginia
Barium	0.1195	0.1077	0.0450	0.0438	0.0703	0.1248	0.1273	0.0910
Beryllium	.0008	.0020	.0007	.0009	.0008	.0006	.0014	.0014
Boron	.0322	.0255	.0140	.0561	.0153	.0247	.0164	.0232
Chromium	.0207	.0260	.0140	.0235	.0244	.0200	.0253	.0222
Cobalt	.0198	.0212	.0150	.0144	.0175	.0136	.0182	.0202
Copper	.0150	.0156	.0075	.0080	.0125	.0116	.0171	.0132
Gallium	.0055	.0099	.0020	.0050	.0071	.0057	.0085	.0077
Germanium	.0046	.0064	.0007	.0059	.0049	.0035	.0041	.0046
Lanthanum	.0138	.0175	.0100	.0126	.0130	.0132	.0151	.0157
Lead	.0040	.0059	.0010	.0043	.0052	.0050	.0078	.0058
Lithium	.0812	.1064	.0140	.0394	.0642	.0994	.0441	.0520
Manganese	.0208	.0361	.0030	.0207	.0205	.0234	.0540	.0249
Molybdenum	.0117	.0071	.0017	.0057	.0098	.0080	.0106	.0073
Nickel	.0186	.0217	.0125	.0203	.0195	.0168	.0281	.0212
Scandium	.0078	.0131	.0065	.0058	.0086	.0141	.0092	.0093
Strontium	.1396	.1538	.0900	.0511	.0943	.1368	.1240	.1104
Tin	.0024	.0063	.0005	.0013	.0011	.0019	.0030	.0017
Vanadium	.0338	.0400	.0225	.0236	.0330	.0354	.0417	.0348
Ytterbium	.0005	.0009	.0003	.0007	.0006	.0006	.0011	.0007
Yttrium	.0126	.0217	.0050	.0150	.0127	.0102	.0151	.0145
Zinc	.0243	.0203	.0200	.0284	.0222	.0242	.0291	.0201
Zirconium	.0607	.0823	.1100	.0805	.0680	.0460	.0559	.0738
Average ash..pct of dry coal	9.2	7.3	9.5	11.8	10.0	9.7	7.8	8.5
Number of samples	47	26	2	85	117	25	51	247

TABLE B-6. AVERAGE TRACE ELEMENT CONTENT IN ASH OF COALS FROM STATES IN INTERIOR PROVINCE, PERCENT OF ASH[4]

Element	Arkansas	Illinois	Indiana	Iowa	Kansas	Missouri	Western Kentucky
Barium	0.1000	0.0423	0.0290	0.0300	0.0150	0.0183	0.0468
Beryllium	.0003	.0011	.0016	.0010	.0005	.0010	.0015
Boron	.0175	.0690	.0803	.0833	.0250	.0667	.0752
Chromium	.0300	.0252	.0182	.0400	.0150	.0433	.0197
Cobalt	.0550	.0131	.0226	.0343	.0450	.0233	.0167
Copper	.0055	.0071	.0091	.0067	.0150	.0108	.0095
Gallium	.0025	.0035	.0035	.0070	.0020	.0065	.0040
Germanium	.0010	.0116	.0139	.0133	.0060	.0088	.0082
Lanthanum	.0300	.0105	.0169	.0133	.0150	.0100	.0115
Lead	.0035	.0279	.0068	.0200	.0100	.0267	.0069
Lithium	.0100	.0386	.0231	.0300	.0050	.0137	.0171
Manganese	.0150	.0621	.0245	.0433	.0300	.0350	.0201
Molybdenum	.0125	.0075	.0049	.0100	.0050	.0108	.0079
Nickel	.0325	.0211	.0308	.0567	.0550	.0767	.0170
Scandium	.0040	.0077	.0074	.0050	.0040	.0047	.0067
Strontium	.2500	.0697	.0660	.0667	.0900	.0417	.0578
Tin	.0012	.0022	.0007	.0009	.0010	.0016	.0027
Vanadium	.0350	.0297	.0327	.0300	.0150	.0375	.0341
Ytterbium	.0003	.0004	.0004	.0008	.0003	.0009	.0005
Yttrium	.0060	.0089	.0098	.0100	.0275	.0142	.0142
Zinc	.0190	.1193	.0690	.1333	.0750	.0620	.0514
Zirconium	.0600	.0755	.0945	.0667	.0750	.0733	.0824
Average ash.....pct of dry coal..	8.3	11.7	10.6	15.5	10.5	12.4	9.3
Number of samples	2	29	31	3	2	6	50

TABLE B-7. AVERAGE TRACE ELEMENT CONTENT IN ASH OF COALS FROM WESTERN STATES, PERCENT OF ASH(4)

Element	Arizona	Colorado	Montana	New Mexico	North Dakota	Utah	Washington	Wyoming
Barium	0.0400	0.0795	0.3000	0.2250	0.2650	0.1122	0.1714	0.1967
Beryllium	.0010	.0006	.0012	.0008	.0002	.0003	.0004	.0028
Boron	.0500	.0494	.0475	.0361	.0337	.0861	.0314	.0417
Chromium	.0100	.0049	.0024	.0091	.0034	.0088	.0121	.0067
Cobalt	0	.0104	.0061	.0126	.0057	.0066	.0217	.0060
Copper	.0050	.0049	.0025	.0050	.0013	.0038	.0121	.0050
Gallium	.0050	.0032	.0039	.0034	.0020	.0030	.0059	.0017
Germanium	.0050	.0019	.0025	.0032	.0006	.0008	.0009	.0018
Lanthanum	0	.0129	.0097	.0150	.0096	.0131	.0133	.0050
Lead	.0040	.0031	.0038	.0040	.0022	.0024	.0025	.0007
Lithium	.0200	.0095	.0215	.0138	.0095	.0283	.0277	.0217
Manganese	.0100	.0216	.0456	.0165	.0300	.0157	.0121	.0160
Molybdenum	.0010	.0018	.0038	.0017	.0032	.0011	.0026	.0025
Nickel	.0050	.0053	.0026	.0069	.0014	.0051	.0114	.0047
Scandium	.0010	.0056	.0034	.0068	.0045	.0037	.0089	.0040
Strontium	.1000	.0974	.2612	.0800	.2612	.1457	.3071	.1167
Tin	.0010	.0023	.0009	.0016	.0013	.0013	.0009	.0012
Vanadium	.0100	.0125	.0097	.0213	.0094	.0117	.0429	.0167
Ytterbium	.0001	.0003	.0004	.0005	.0004	.0002	.0004	.0003
Yttrium	.0100	.0083	.0060	.0085	.0060	.0067	.0094	.0053
Zinc	.0100	.0362	.0337	.0164	.0250	.0109	.0243	.0425
Zirconium	.0400	.0872	.0612	.0914	.0662	.0861	.1286	.0450
Average ash..pct of dry coal.	9.7	9.2	12.6	11.8	12.0	7.0	12.7	8.7
Number of samples	1	40	8	14	8	23	7	3

TABLE B-8. RANGE IN AMOUNT OF TRACE ELEMENTS PRESENT IN COAL ASHES (ppm) (5)

	Anthracites			High volatile bituminous		
Element	Max.	Min.	Average (5)	Max.	Min.	Average (24)
Ag	1	1	*	3	1	*
B	130	63	90	2800	90	770
Ba	1340	540	866	4660	210	1253
Be	11	6	9	60	4	17
Co	165	10	81 (4)	305	12	64
Cr	395	210	304	315	74	193
Cu	540	96	405	770	30	293
Ga	71	30	42	98	17	40
Ge	20	20	*	285	20	*
La	220	115	142	270	29	111
Mn	365	58	270	700	31	170
Ni	320	125	220	610	45	154
Pb	120	41	81	1500	32	183
Sc	82	50	61	78	7	32
Sn	4250	19	962	825	10	171 (22)
Sr	340	80	177	9600	170	1987
V	310	210	248	840	60	249
Y	120	70	106	285	29	102
Yb	12	5	8	15	3	10
Zn	350	155	*	1200	50	310 (14)
Zr	1200	370	688	1450	115	411

* = Insufficient figures to compute an average value.

O = Figures encircled indicate the number of samples used to compute average values.

TABLE B-8. (CONTINUED)

	Low Volatile Bituminous			Medium Volatile Bituminous		
Element	Max.	Min.	Average (8)	Max.	Min.	Average (7)
Ag	1.4	1	*	1	1	*
B	180	76	123	780	74	218
Ba	2700	96	740	1800	230	896
Be	40	6	16	31	4	13
Co	440	26	172	290	10	105(6)
Cr	490	120	221	230	36	169
Cu	850	76	379	560	130	313
Ga	135	10	41(7)	52	10	*
Ge	20	20	*	20	20	*
La	180	56	110	140	19	83
Mn	780	40	280	4400	125	1432
Ni	350	61	141	440	20	263(6)
Pb	170	23	89	210	52	96
Sc	155	15	50	110	7	56
Sn	230	10	92(7)	160	29	75
Sr	2500	66	818	1600	40	668
V	480	115	278	860	170	390
Y	460	37	152	340	37	151
Yb	23	4	10	13	4	9
Zn	550	62	231	460	50	195(6)
Zr	620	220	458	540	180	326

* = Insufficient figures to compute an average value.
O = Figures encircled indicate the number of samples used to compute an average value.

TABLE B-8. (CONTINUED)

Lignites and Subbituminous			
Element	Max.	Min.	Average (13)
Ag	50	1	*
B	1900	320	1020
Ba	13900	550	5027
Be	28	1	6
Co	310	11	45
Cr	140	11	54
Cu	3020	58	655
Ga	30	10	23 (12)
Ge	100	20	*
La	90	34	62
Mn	1030	310	688
Ni	420	20	129 8
Pb	165	20	60
Sc	58	2	18 (10)
Sn	660	10	156
Sr	8000	230	4660
V	250	20	125
Y	120	21	51
Yb	10	2	4
Zn	320	50	*
Zr	490	100	245

*=Insufficient figures to compute an average value.

O =Figures encircled indicate the number of samples used to compute average values.

TABLE B-9. CONCENTRATIONS OF TRACE ELEMENTS IN COAL FLY ASH AND FLUE GAS (ppm) (1)

Element	Concn in coal	Source[a]	Control method[b]	Concn in fly ash		Concn suspended in flue gas		Analytical method
				Before control	After control	Before control	After control	
Antimony	-	A	ESP	-	-	265	58	OES-P
	<700	IE	Mech	<600	<600	-	-	-
	-	IE	ESP	-	-	689	6.8	AAS
	-	IE	Cy	-	17-53	-	-	SSMS
	0.72-1.4	-	ESP	-	-	-	1.7±0.5	INAA
	-	SW	ESP	-	18	-	-	XRF
	-	SW	WS	14	22	-	-	XRF
	0.5	IE	ESP	12	55	-	-	INAA
Arsenic	5.44	Av U.S.	-	-	147	-	-	OES
	-	A	ESP	-	-	414	193	OES-P
	-	A	ESP	-	-	1513	47	OES-P
	-	IE	Cy	-	680-1700	-	-	AAS
	20-32	-	ESP	-	-	-	72±18	PAA
	-	SW	ESP	-	150	-	-	XRF
	-	SW	WS	130	280	-	-	XRF
	14	IE	ESP	120	440	-	-	INAA
Barium	-	A	ESP	-	-	1644	26	OES-P
	<300	IE	Mech	<400	<400	-	-	-
	130-210	-	ESP	-	-	-	72 ±44	INAA
	59	IE	ESP	450	750	-	-	INAA
Beryllium	-	A	ESP	-	-	32	6	OES-P
	<2	IE	Mech	10	10	-	-	-
	-	IE	Cy	-	34-60	-	-	OES
	<5	IE	ESP	3-17	<10	-	-	SSMS
Boron	-	A	ESP	-	-	1573	66	OES-P
	100-200	IE	ESP	250-3000	150-300	-	-	SSMS
Bromine	32-45	-	ESP	-	-	-	2.2±0.5	INAA
Cadmium	-	-	ESP	-	<20-170	-	-	OES
	-	A	ESP	-	-	232	54.5	OES-P
	6	IE	Mech	160	20	-	-	-
	-	IE	ESP	-	-	8.5	0.1	FAAS
	-	IE	Cy	-	13-35	-	-	AAS
	0.46	IE	ESP	8.0	51	-	-	SSMS-ID
Chlorine	355-407	IE	ESP	<5-50	1000	-	-	INAA

TABLE B-9. (CONTINUED)

Element	Concn in coal	Source[a]	Control method[b]	Concn in fly ash		Concn suspended in flue gas		Analytical method
				Before control	After control	Before control	After control	
Chromium	-	A	ESP	-	-	1674	20	OES-P
	20	IE	Mech	500	7400	-	-	-
	-	IE	ESP	-	-	300	0.7	PAAS
	-	IE	Cy	-	290-3300	-	-	AAS
	25-35	-	ESP	-	-	-	13.8±5.1	INAA
	20	IE	ESP	310	900	-	-	INAA
Cobalt	-	A	ESP	-	-	227	20	OES-P
	0	IE	Mech	60	70	-	-	-
	-	IE	Cy	-	60-130	-	-	OES
	4.9-6.2	-	ESP	-	-	-	3.4±2.1	INAA
	3.0	IE	ESP	41	65	-	-	INAA
Copper	-	A	ESP	-	-	620	48	OES-P
	20	IE	Mech	100	200	-	-	-
	-	IE	Cy	-	270-390	-	-	SSMS
	9.6	SW	ESP	-	320	-	-	XRF
	9.6	SW	WS	280	290	-	-	XRF
	50-100	IE	ESP	300-400	200-400	-	-	SSMS
Fluorine	<2-60	-	-	<10-100	-	-	-	SSMS
Iodine	25-64	-	ESP	-	-	-	28.3±3.1	INAA
Lead	-	A	ESP	-	-	649	94	OES-P
	<30	IE	Mech	200	200	-	-	-
	-	IE	Cy	-	1100-1600	-	-	AAS
	6.5-12.4	-	ESP	-	-	-	13.8±2.8	PAA
	-	SW	ESP	-	130	-	-	XRF
	-	SW	WS	110	340	-	-	XRF
	4.9	IE	ESP	80	650	-	-	SSMS-ID
Manganese	-	-	ESP	-	465	-	-	OES
	-	A	ESP	-	-	1362	23	OES-P
	90	IE	Mech	500	800	-	-	-
	-	IE	Cy	-	150-470	-	-	OES
	31-45	-	ESP	-	-	-	25±13	INAA
	34	IE	ESP	290	430	-	-	INAA
Mercury	0.11 0.63	SE	Mech[d]	-	-	-	62	PASS
	0.11-0.63	SE	ESP	-	-	-	43	PASS
	0.33	-	ESP	-	0.4	-	31	INAA/ASV/PES
	-	A	ESP	-	-	89	15	OES-P
	<2	IE	Mech	<0.2	20	-	-	-
	0.122	IE	ESP	0.05	-	-	-	PASS

TABLE B-9. (CONTINUED)

Element	Concn in coal	Source[a]	Control method[b]	Concn in fly ash		Concn suspended in flue gas		Analytical method[c]
				Before control	After control	Before control	After control	
Molybdenum	-	A	ESP	-	-	181	13	OES-P
	<20	IE	Mech	<30	<30	-	-	-
	0.99	SW	ESP	-	60	-	-	XRF/WC
	0.99	SW	WS	54	110	-	-	XRF/WC
	3.6	IE	ESP	118	-	-	-	INAA
Nickel	10-30	-	ESP	-	50-290	-	-	OES
	-	A	-	-	-	792	18	OES-P
	90	IE	Mech	500	2000	-	-	-
	-	IE	ESP	-	-	395	1.3	FAAS
	-	IE	Cy	-	460-1600	-	-	AAS
	21-42	-	ESP	-	-	-	15.4±6.1	PAA
	<100-150	IE	ESP	500-1000	500-1000	-	-	SSMS
Selenium	<600	IE	Mech	<500	<500	-	-	-
	-	IE	ESP	-	-	114	6.5	INAA
	-	IE	Cy	-	11-59	-	-	FAAS
	2.8-7.8	-	ESP	-	-	-	12±5	INAA
	1.9	SW	ESP	73	62	-	-	XRF
	1.9	SW	WS	73	440	-	-	XRF
	2.2	IE	ESP	25	88	-	-	GC-MES
Tellurium	1-3	IE	ESP	<1-10	<1-10	-	-	SSMS
Thallium	<100	IE	Mech	100	50	-	-	-
	-	IE	Cy	-	29-76	-	-	SSMS
	2	IE	ESP	40-100	30	-	-	SSMS
Tin	-	A	ESP	-	-	570	61	OES-P
	<700	IE	Mech	<600	<600	-	-	-
	-	IE	Cy	-	7-19	-	-	SSMS
	20	IE	ESP	20	20	-	-	SSMS
Titanium	-	A	ESP	-	-	16320	264	OES-P
	<980	IE	Mech	5800	6600	-	-	-
	-	IE	Cy	-	9200-15900	-	-	XRF
	900-1450	IE	ESP	6080	10000	-	480±260	INAA
	510	IE	ESP			-	-	INAA

TABLE B-9. (CONTINUED)

Element	Conc in coal	Source[a]	Control method[b]	Concn in fly ash		Concn suspended in flue gas		Analytical method[c]
				Before control	After control	Before control	After control	
Vanadium	22.5	-	ESP/WS	116	-	-	-	OES
	-	A	ESP	-	-	2842	14	OES-P
	<200	IE	Mech	200	300	-	-	-
	-	IE	ESP	-	-	970	1.5	FAAS
	-	IE	Cy	-	150-480	-	-	SSMS
	37-46	-	ESP	-	-	-	27±32	INAA
	28.5	IE	ESP	440	1180	-	-	INAA
Zinc.	1100	IE	Mech	5900	900	-	-	-
	-	IE	ESP	-	-	162	0.7	AAS
	55-110	-	ESP	-	-	-	43±23	INAA
	-	IE	Cy	-	8100-13000	-	11340-18200	SSMS
	7.3	SW	ESP	-	370	-	-	FAAS
	7.3	SW	WS	360	600	-	-	FAAS
	46	IE	ESP	740	5900	-	-	SSMS-ID

a. Control equipment:
Mech = Mechanical collector
Cy = Cyclone collector
ESP = Electrostatic precipitator
WS = Wet scrubber

b. Sample was collected upstream from the mechanical collector.

c. Abbreviations for analytical methods.

OES = Optical Emission Spectroscopy-Detection Method Unspecified
OES-P = Optical Emission Spectroscopy with Photographic Detection
FAAS = Flameless Atomic Absorption Spectroscopy
SSMS = Spark Source Mass Spectroscopy
INAA = Instrumental Neutron Activation Analysis
AAS = Atomic Absorption Spectroscopy
SSMS-ID = Spark Source Mass Spectroscopy with Isotope Dilution

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